Supporting Information

A Supramolecular Ladder Polymer by Hydrogen Bonding-Mediated Self-Assembly of a Metallomacrocycle

Chun-Fai Ng and Hak-Fun Chow*

Department of Chemistry and Institute of Molecular Functional Materials, UGC-AoE, The Chinese University of Hong Kong, Shatin, Hong Kong SAR

Email address: hfchow@cuhk.edu.hk

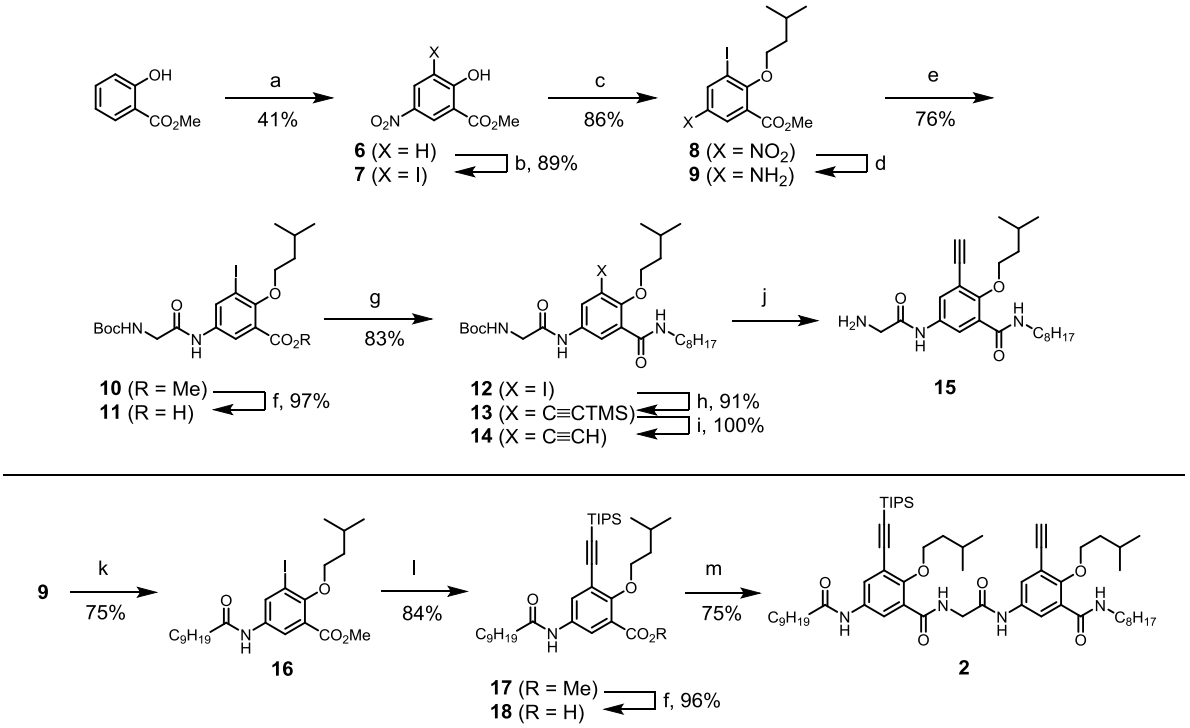
Table of content

Synthesis

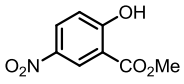
1.1 General. All reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium/benzophenone ketyl under nitrogen before use. CH_2Cl_2 was freshly distilled from CaH_2. Dimethylformamide (DMF) and diisopropylamine (DIPA) were dried with $MgSO_4$ and distilled prior to use. All reactions were carried out under N_2 atmosphere unless otherwise stated. All reactions were monitored by thin layer chromatographic analysis on pre-coated silica gel plates, which were visualized by UV lamp at 254 or 365 nm and/or stained using 5% (w/v) dodecamolybdophosphoric acid in ethanol followed by heating. Flash column chromatography was performed on glass column of silica gel (230–400 mesh) and solvent ratios were expressed in volume to volume.

^1H, ^{13}C, ^{31}P, COSY, HSQC and ROESY NMR spectra for structural characterization were recorded either on a 400 MHz nuclear magnetic resonance spectrometer (^1H: 400 MHz; ^{13}C: 100 MHz; ^{31}P: 162 MHz) or a 700 MHz nuclear magnetic resonance spectrometer (^1H: 700 MHz; ^{13}C: 176 MHz) as specified. ^1H NMR spectra for concentration dependent studies were recorded on a 700 MHz nuclear magnetic resonance spectrometer. Unless otherwise stated, all NMR measurements were conducted in $CDCl_3$ at 25 °C. Chemical shifts were reported as parts per million in δ scale using solvent residual peak as internal standard for ^1H and ^{13}C NMR, whereas the signal of PPh_3 was used as external standard for ^{31}P NMR spectroscopy. Tetramethylsilane was used as an internal standard for mixed solvent system. Coupling constants (*J*) were reported in hertz. All mass spectra were obtained on a double focusing sector mass spectrometer using electron spray ionization (ESI) technique. The reported molecular mass (*m/z*) values were monoisotopic mass unless otherwise stated. Melting points were measured on a digital melting point apparatus and were uncorrected.

1.2 Synthesis of DADA quadruple H-bonding array **2** – The synthetic scheme of compound **2** is shown in Scheme S1.



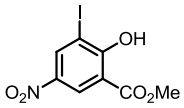
Scheme S1. Reagent and conditions: (a) conc. HNO_3, CH_3CO_2H, 12 h; (b) Ag_2SO_4, I_2, CH_3OH; 3 h; (c) isoamyl bromide, K_2CO_3, DMF, 24 h; (d) $Na_2S_2O_4$, THF, H_2O, 2 h; (e) Boc-Gly-OH, EDCI, HOBt, CH_2Cl_2, 30 min; then compound **9**, CH_2Cl_2, 12 h; (f) KOH, THF, H_2O, 12 h; (g) EDCI, HOBt, CH_2Cl_2, 30 min, then *n*-octylamine, CH_2Cl_2, 12 h; (h) TMSC≡CH, $PdCl_2(PPh_3)_2$, cat. CuI, Et_3N, THF, 50 °C, 12 h; (i) TBAF, THF, 10 min; (j) TFA, CH_2Cl_2, 1 h; (k) $C_9H_{19}CO_2H$, EDCI, HOBt, CH_2Cl_2, 30 min, then compound **9**, CH_2Cl_2, 12 h; (l) TIPSC≡CH, $PdCl_2(PPh_3)_2$, cat. CuI, Et_3N, THF, 50 °C, 12 h; (m) EDCI, HOBt, CH_2Cl_2, 30 min, then compound **15**, CH_2Cl_2, 12 h.



6

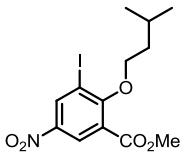
Compound 6.[S1] A mixture of methyl salicylate (10.10 g, 66.38 mmol), glacial acetic acid (30 mL) and concentrated nitric acid (10 mL) were stirred at 25 °C for 12 h. The reaction mixture was then concentrated under reduced pressure and subjected to flash column chromatography (hexane/EtOAc = 15/1) to afford compound **6** (5.37 g, 27.22 mmol, 41%) as a white solid. M.p.: 117–118 °C; R_f: 0.47 (hexane/EtOAc = 6/1); ^{1}H NMR: 11.41 (s, OH, 1 H), 8.75 (d, J = 2.7, ArH, 1 H), 8.30 (dd, J = 9.2, 2.7, ArH, 1 H), 7.06 (d, J = 9.2, ArH, 1 H), 4.02 (s, CO_2CH_3, 3 H); ^{13}C NMR: 169.4, 166.3, 140.1, 130.6, 126.7, 118.7, 112.2, 53.2; *m/z* (ESI) 220 ($M + Na^+$, 100%), HRMS (ESI) calcd for $C_8H_7NO_5 + Na^+$: 220.0216, found: 220.0212.

[S1] N. Y. Mok, J. Chadwick, K. A. B. Kellett, N. M. Hooper, A. P. Johnson, C. W. G. Fishwick, *Bioorg. Med. Chem. Lett.* **2009**, *19*, 6770.



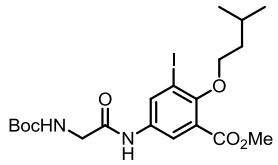
7

Compound 7. Silver sulfate (1.91 g, 6.12 mmol) and iodine (1.42 g, 5.58 mmol) were added to a solution of **6** (1.10 g, 5.58 mmol) in methanol (50 mL). The reaction mixture was stirred at 25 °C for 3 h. The reaction mixture was filtered and washed with methanol. The filtrate was evaporated *in vacuo* to give a crude yellow solid which was purified by recrystallization from hexane and EtOAc to give compound **7** (1.60 g, 4.97 mmol, 89%) as a pale yellow needle crystal. M.p.: 148–149 °C; R_f: 0.40 (hexane/EtOAc = 6/1); ^{1}H NMR: 12.29 (s, OH, 1 H), 8.77 (d, J = 2.8, ArH, 1 H), 8.75 (d, J = 2.8, ArH, 1 H), 4.05 (s, CO_2CH_3, 3 H); ^{13}C NMR: 169.0, 165.1, 140.5, 139.7, 126.3, 111.5, 85.3, 53.8; *m/z* (ESI) 324 (M + H^+, 100%). HRMS calcd for $C_8H_6INO_5$ + H^+: 323.9363, found: 323.9363.



8

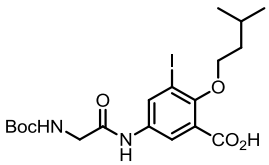
Compound 8. A mixture of 1-bromo-3-methylbutane (0.51 g, 3.41 mmol), compound **7** (1.00 g, 3.10 mmol) and potassium carbonate (1.07 g, 7.74 mmol) was stirred in dry DMF (50 mL) at 80 °C for 24 h. The reaction was then cooled to 25 °C and DMF was evaporated *in vacuo*. The yellow residue was diluted with EtOAc (50 mL) and the organic phase was washed with saturated Na_2CO_3 followed by brine, dried ($MgSO_4$) and filtered. The filtrate was concentrated *in vacuo* and the residue purified by flash chromatography (hexane/EtOAc = 10/1) to afford the target compound **8** (1.05 g, 2.66 mmol, 86%) as a pale yellow oil. R_f: 0.60 (hexane/EtOAc = 6/1); ^{1}H NMR: 8.79 (d, J = 2.8, ArH, 1 H), 8.65 (d, J = 2.8, ArH, 1 H), 4.10 (t, J = 6.6, OCH_2, 2 H), 3.97 (s, CO_2CH_3, 3 H), 1.96–1.86 (m, $(CH_3)_2CH$, 1 H), 1.82–1.77 (m, OCH_2CH_2, 2 H), 0.99 (d, J = 6.6, $(CH_3)_2C$, 6 H); ^{13}C NMR: 163.8, 163.5, 143.2, 137.6, 127.3, 124.9, 94.1, 74.9, 53.0, 38.8, 24.8, 22.6; *m/z* (ESI) 416 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{13}H_{16}INO_5$ + Na^+: 415.9965, found: 415.9969.



10

Compound 10.[S2] Compound **8** (0.21 g, 0.53 mmol) was added to a solution of $Na_2S_2O_4$ (0.93 g, 5.34 mmol) in THF (20 mL) and H_2O (20 mL). The reaction mixture was stirred at 25 °C for 2 h. The solvent was evaporated *in vacuo* and the residue extracted with EtOAc (3 × 50 mL). The organic phase was washed with brine, dried ($MgSO_4$), filtered and the solvent evaporated to give the crude amine **9** which was used in the next step without further purification.

1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide methiodide (EDCI) (0.18 g, 0.64 mmol) and 1-hydroxybenzotriazole (HOBt) (87 mg, 0.64 mmol) were added to a solution of Boc-glycine (0.10 g, 0.59 mmol) in CH_2Cl_2 (30 mL). After 30 min, a solution of the crude amine **9** in CH_2Cl_2 (10 mL) was then added and the reaction mixture was stirred at 25 °C for 12 h. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography ($CHCl_3$/CH_3OH/Et_3N = 250/10/1) to afford compound **10** (0.21 g, 0.41 mmol, 76% in 2 steps) as a white solid. M.p.: 144–145 °C; R_f: 0.27 ($CHCl_3$/CH_3OH/Et_3N 200/10/1); ^{1}H NMR: 8.51 (br s, NH, 1 H), 8.22 (s, ArH, 1 H), 7.85 (d, J = 2.4, ArH, 1 H), 5.36 (br s, N*H*Boc, 1 H), 3.95–3.92 (m, 4 H), 3.89 (s, CO_2CH_3, 3 H), 1.93–1.71 (m, 3 H), 1.47 (s, $C(CH_3)_3$, 9 H), 0.97 (d, J = 6.6, $(CH_3)_2C$, 6 H); ^{13}C NMR: 168.1, 165.5, 156.7, 154.9, 134.6, 134.4, 125.2, 123.3, 94.4, 80.8, 74.1, 52.6, 45.2, 38.9, 28.4, 24.9, 22.9; *m/z* (ESI) 543 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{20}H_{29}IN_2O_6 + Na^+$: 543.0963, found: 543.0959; Anal. $C_{20}H_{29}IN_2O_6$ requires C, 46.16; H, 5.62; N, 5.38%; found: C, 46.15; H, 5.57; N, 5.34%.

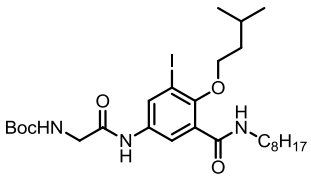


11

Compound 11. A mixture of compound **10** (0.23 g, 0.44 mmol) and aqueous KOH solution (2.5 M, 10 mL) in THF (30 mL) was stirred at 25 °C for 12 h. The reaction mixture was concentrated *in vacuo* and acidified with saturated NH_4Cl solution (50 mL). The mixture was then extracted with EtOAc (3 × 50 mL) and the combined extracts were washed with brine, dried ($MgSO_4$), filtered and evaporated *in vacuo* to give a pale yellow solid which was purified

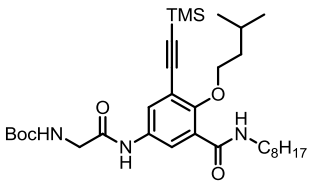
[S2] J. M. Khurana, S. Singh, *J. Indian Chem. Soc.* **1996**, *73*, 487.

by recrystallization from hexane and EtOAc to afford the target compound **11** (0.22 g, 0.43 mmol, 97%) as a white solid. M.p.: 161–162 °C; R_f: 0.10 (hexane/EtOAc = 1/1); ^{1}H NMR (CD_3OH): CO_2H signal was too broad to be observed, 9.91 (br s, NH, 1 H), 8.21 (br s, ArH, 1 H), 7.79 (br s, ArH, 1 H), 6.86 (br s, N*H*Boc, 1 H), 3.98 (t, J = 6.1, OCH_2, 2 H), 3.86 (d, J = 4.8, C*H*$_2$NHBoc, 2 H), 1.89–1.84 (m, $(CH_3)_2$C*H*, 1 H), 1.73–1.70 (m, OCH_2CH_2, 2 H), 1.44 (s, $C(CH_3)_3$, 9 H), 0.96 (d, J = 6.5, $(CH_3)_2$C, 6 H); ^{13}C NMR (CD_3OH): 170.6, 170.2, 158.4, 154.6, 136.2, 134.0, 130.0, 123.3, 93.9, 80.6, 74.5, 45.0, 39.9, 28.6, 25.8, 23.0; *m/z* (ESI) 529 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{19}H_{27}IN_2O_6$ + Na^+: 529.0806, found: 529.0804.



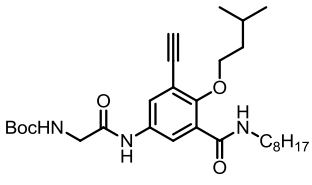
12

Compound 12. EDCI (0.16 g, 0.54 mmol) and HOBt (71 mg, 0.52 mmol) were added to a solution of compound **11** (0.24 g, 0.47 mmol) in CH_2Cl_2 (30 mL) and stirred at 25 °C. After 30 min, octylamine (0.12 g, 0.95 mmol) was added and the reaction mixture was stirred at 25 °C for 12 h. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography (hexane/EtOAc/Et_3N = 100/100/1) to afford compound **12** (0.24 g, 0.39 mmol, 83%) as a white solid. M.p.: 138–139 °C; R_f: 0.67 (hexane/EtOAc/Et_3N = 200/100/1); ^{1}H NMR: 8.58 (d, J = 2.6, ArH, 1 H), 8.47 (br s, NH, 1 H), 7.76 (d, J = 2.7, ArH, 1 H), 7.73 (t, J = 5.2, NH, 1 H), 5.25 (br s, N*H*Boc, 1 H), 3.94 (d, J = 5.9, C*H*$_2$NHBoc, 2 H), 3.90 (t, J = 7.0, OCH_2, 2 H), 3.45 (q, J = 7.0, CONHC*H*$_2$, 2 H), 1.86–1.74 (m, 3 H), 1.63–1.58 (m, 2 H), 1.48 (s, $C(CH_3)_3$, 9 H), 1.38–1.27 (m, 10 H), 0.98 (d, J = 6.4, $CH(CH_3)_2$, 6 H), 0.88 (t, J = 7.0, CH_3, 3 H); ^{13}C NMR: 168.3, 164.4, 156.4, 152.6, 135.7, 133.9, 127.6, 122.9, 93.2, 80.3, 74.6, 45.0, 40.3, 39.0, 31.9, 29.6, 29.4, 29.3, 28.4, 27.2, 25.1, 22.9, 22.7, 14.2; *m/z* (ESI) 640 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{27}H_{44}IN_3O_5$ + Na^+: 640.2218, found: 640.2227; Anal. $C_{27}H_{44}IN_3O_5$ requires C, 52.51; H, 7.18; N, 6.80%; found: C, 52.52; H, 7.04; N, 6.71%.



13

Compound 13.[S3] A mixture of compound **12** (0.21 g, 0.34 mmol), trimethylsilylacetylene (0.24 mL, 1.70 mmol), CuI (7 mg, 34.0 μmol), $Pd(PPh_3)_2Cl_2$ (24 mg, 34.0 μmol) and Et_3N (0.5 mL) in dry THF (20 mL) was frozen in a sealed tube under liquid N_2 and degassed with N_2 (3 ×). The mixture was then stirred at 50 °C for 12 h. The reaction mixture was filtered through a short pad of Celite and washed with Et_2O (20 mL). The filtrate was concentrated *in vacuo* and the residue purified by flash chromatography (hexane/EtOAc/Et_3N = 200/100/1) to afford compound **13** (0.18 g, 0.31 mmol, 91%) as a white solid. M.p.: 105–106 °C; R_f: 0.67 (hexane/EtOAc/Et_3N = 200/100/1); ^{1}H NMR: 8.62 (br s, NH, 1 H), 8.26 (d, *J* = 2.8, ArH, 1 H), 8.05 (t, *J* = 5.2, NH, 1 H), 7.80 (d, *J* = 2.8, ArH, 1 H), 5.31 (br s, N*H*Boc, 1 H), 4.16 (t, *J* = 7.0, OCH_2, 2 H), 3.96 (br s, C*H*$_2$NHBoc, 2 H), 3.44 (q, *J* = 6.9, CONHC*H*$_2$, 2 H), 1.82–1.71 (m, 3 H), 1.62–1.55 (m, 2 H), 1.47 (s, $C(CH_3)_3$, 9 H), 1.37–1.27 (m, 10 H), 0.97 (d, *J* = 6.3, $CH(CH_3)_2$, 6 H), 0.87 (t, *J* = 7.0, CH_3, 3 H), 0.26 (s, $(CH_3)_3Si$, 9 H); ^{13}C NMR: 168.3, 164.6, 156.3, 154.8, 134.2, 128.9, 126.7, 123.0, 118.6, 100.4, 100.2, 80.1, 74.3, 44.9, 40.2, 39.1, 31.9, 29.5, 29.4, 29.3, 28.4, 27.2, 25.2, 22.8, 22.7, 14.2, –0.1; *m/z* (ESI) 610 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{32}H_{53}N_3O_5Si + Na^+$: 610.3647, found: 610.3647; Anal. $C_{32}H_{53}N_3O_5Si$ requires C, 65.38; H, 9.09; N, 7.14%; found: C, 65.50; H, 9.21; N, 7.09%.

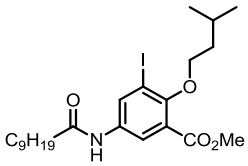


14

Compound 14. A mixture of tetrabutylammonium fluoride (TBAF) in THF (1 M, 0.4 mL) and compound **13** (0.18 g, 0.31 mmol) in THF (20 mL) was stirred at 25 °C for 10 min. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography (hexane/EtOAc/Et_3N = 200/100/1 gradient to EtOAc/Et_3N = 100/1) to afford compound **14** (0.15 g, 0.31 mmol, 100%) as a pale yellow foam. R_f: 0.57 (hexane/EtOAc/Et_3N = 200/100/1); ^{1}H NMR: 8.80 (br s, N*H*Boc, 1 H), 8.27 (d, *J* = 2.8, ArH, 1 H), 8.03 (t, *J* = 5.2, NH, 1 H), 7.86

[S3] K. Sonogashira, Y. Tohda, N. Hagihara, *Tetrahedron Lett.* **1975**, *50*, 4467.

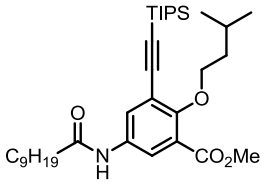
(d, J = 2.8, ArH, 1 H), 5.41 (br s, N*H*Boc, 1 H), 4.15 (t, J = 7.0, OCH_2, 2 H), 3.98 (d, J = 5.1, CH_2NHBoc, 2 H), 3.44 (q, J = 7.0, CONHCH_2, 2 H), 3.32 (s, C≡CH, 1 H), 1.86–1.69 (m, 3 H), 1.63–1.55 (m, 2 H), 1.46 (s, $C(CH_3)_3$, 9 H), 1.37–1.24 (m, 10 H), 0.96 (d, J = 6.4, $CH(CH_3)_2$, 6 H), 0.87 (t, J = 7.0, CH_3, 3 H); ^{13}C NMR: 168.4, 164.5, 156.3, 154.9, 134.3, 128.8, 126.8, 123.3, 117.4, 82.5, 79.8, 79.3, 74.3, 44.8, 40.1, 39.0, 31.8, 29.5, 29.3, 29.2, 28.3, 27.2, 25.0, 22.7, 22.6, 14.1; *m/z* (ESI) 538 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{29}H_{45}N_3O_5$ + Na^+: 538.3251, found: 538.3248.



16

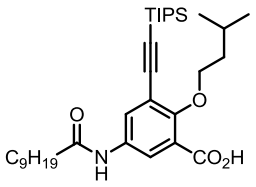
Compound 16. Compound **8** (0.34 g, 0.86 mmol) was added to a solution of $Na_2S_2O_4$ (1.51 g, 8.65 mmol) in a mixture of THF (20 mL) and H_2O (20 mL). The reaction mixture was stirred at 25 °C for 2 h. The solvent was evaporated *in vacuo* and the residue extracted with EtOAc (3 × 50 mL). The organic phase was washed with brine, dried ($MgSO_4$) and filtered. The solvent was evaporated and the crude amine **9** was used in the next step without further purification.

EDCI (0.28 g, 0.95 mmol) and HOBt (0.13 g, 0.95 mmol) were added to a solution of decanoic acid (0.16 g, 0.95 mmol) in CH_2Cl_2 (30 mL). After 30 min, a solution of the crude amine **9** in CH_2Cl_2 (10 mL) was then added and the reaction mixture stirred at 25 °C for 12 h. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography (hexane/EtOAc = 3/1) to afford compound **16** (0.34 g, 0.65 mmol, 75% in 2 steps) as a white solid. M.p.: 59–60 °C; R_f: 0.33 (hexane/EtOAc = 6/1); ^{1}H NMR: 8.25 (d, J = 2.5, ArH, 1 H), 7.83 (d, J = 2.6, ArH, 1 H), 7.42 (br s, NH, 1 H), 3.93 (t, J = 6.8, OCH_2, 2 H), 3.88 (s, CO_2CH_3, 3 H), 2.33 (t, J = 7.5, CH_2CONH, 2 H), 1.92–1.82 (m, $(CH_3)_2$C*H*, 1 H), 1.77–1.65 (m, 4 H), 1.30–1.25 (m, 12 H), 0.97 (d, J = 6.6, $CH(CH_3)_2$, 6 H), 0.87 (t, J = 6.6, CH_3, 3 H); ^{13}C NMR: 172.4, 165.5, 154.6, 135.0, 134.7, 125.0, 123.2, 94.2, 74.0, 52.5, 38.9, 37.4, 31.9, 29.51, 29.47, 29.34, 29.32, 25.6, 24.9, 22.8, 22.7, 14.2; *m/z* (ESI) 540 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{23}H_{36}INO_4$ + Na^+: 540.1581, found: 540.1577; Anal. $C_{23}H_{36}INO_4$ requires C, 53.39; H, 7.01; N, 2.71%; found: C, 53.62; H, 7.40; N, 2.69%.



17

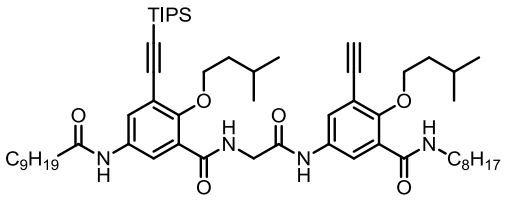
Compound 17. A mixture of compound **16** (0.73 g, 1.41 mmol), triisopropylsilylacetylene (0.95 mL, 4.23 mmol), CuI (27 mg, 0.14 mmol), $Pd(PPh_3)_2Cl_2$ (99 mg, 0.14 mmol) and Et_3N (2 mL) in dry THF (30 mL) was frozen in a sealed tube under liquid N_2 and degassed with N_2 (3 ×). The mixture was then stirred at 50 °C for 12 h. The reaction mixture was filtered through a short pad of Celite and then washed with Et_2O (20 mL). The filtrate was concentrated *in vacuo* and the residue purified by flash chromatography (hexane/$CHCl_3$ = 1/3 gradient to $CHCl_3$) to afford compound **17** (0.68 g, 1.19 mmol, 84%) as a yellow oil. R_f: 0.30 (hexane/$CHCl_3$ = 1/3); ^{1}H NMR: 7.83 (d, J = 2.4, ArH, 1 H), 7.80 (d, J = 2.5, ArH, 1 H), 7.07 (br s, NH, 1 H), 4.14 (t, J = 7.0, OCH_2, 2 H), 3.88 (s, $COCH_3$, 3 H), 2.33 (t, J = 7.5, C*H*$_2$CONH, 2 H), 1.81–1.67 (m, 5 H), 1.33–1.25 (m, 12 H), 1.13 (s, $(CH_3)_2CH$ + $(CH_3)_2CH$, 21 H), 0.93 (d, J = 6.3, $CH(CH_3)_2$, 6 H), 0.87 (t, J = 6.4, CH_3, 3 H); ^{13}C NMR: 172.4, 165.5, 154.6, 135.0, 134.7, 125.0, 123.2, 94.2, 74.0, 52.5, 38.9, 37.4, 31.9, 29.51, 29.47, 29.33, 29.32, 25.6, 24.9, 22.8, 22.7, 14.2; *m/z* (ESI) 594 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{34}H_{57}NO_4Si$ + Na^+: 594.3949, found: 594.3951.



18

Compound 18. A mixture of the ester **17** (0.67 g, 1.17 mmol) in THF (30 mL) and aqueous KOH solution (2.5 M, 10 mL) was stirred at 25 °C for 12 h. The reaction mixture was concentrated *in vacuo* and acidified with saturated NH_4Cl solution (50 mL). The mixture was extracted with EtOAc (3 × 50 mL) and the combined extracts washed with brine, dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the acid **18** (0.63 g, 1.12 mmol, 96%) as a pale yellow solid. M.p.: 104–106 °C; R_f: 0.40 ($CHCl_3$/CH_3OH/Et_3N = 200/10/1); ^{1}H NMR: 11.49 (br s, CO_2H, 1 H), 8.55 (d, J = 2.2, ArH, 1 H), 8.28 (s, NH, 1 H), 7.97 (d, J = 2.6, ArH, 1 H), 4.49 (t, J = 7.1, OCH_2, 2 H), 2.43 (t, J = 7.5, C*H*$_2$CONH, 2 H), 1.78–1.68 (m, 5 H), 1.38–1.25 (m, 12 H), 1.14 (s, $(CH_3)_2CHSi$ + $(CH_3)_2CHSi$, 21 H), 0.94 (d, J = 6.2, $CH(CH_3)_2$, 6 H), 0.86 (t, J = 6.2, CH_3, 3 H); ^{13}C NMR: 172.7, 165.8, 154.9, 135.6, 131.3, 123.4, 121.7, 118.3, 101.4, 98.9, 75.5, 38.5, 37.6, 32.0, 29.6, 29.5, 29.40, 29.37, 25.7, 25.2, 22.8, 22.7, 18.8, 14.2,

11.4; *m/z* (ESI) 580 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{33}H_{55}NO_4Si$ + Na^+: 580.3793, found: 580.3796.

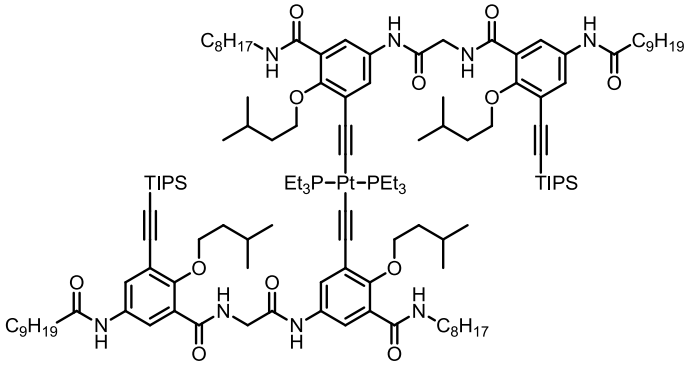


2

Compound 2. A mixture of trifluoroacetic acid (3 mL) and compound **14** (0.27 g, 0.52 mmol) in CH_2Cl_2 (30 mL) was stirred at 25 °C for 1 h. The reaction mixture was then neutralized with saturated Na_2CO_3 solution and extracted with CH_2Cl_2 (3 × 50 mL). The combined extracts were washed with brine, dried ($MgSO_4$), filtered and evaporated *in vacuo* to give the crude amine **15** which was used for next step without further purification.

EDCI (0.17 g, 0.58 mmol) and HOBt (78 mg, 0.58 mmol) were added to a solution of the acid **18** (0.29 g, 0.52 mmol) in CH_2Cl_2 (30 mL). After 30 min, a solution of the amine **15** in CH_2Cl_2 (10 mL) was then added and the reaction mixture stirred at 25 °C for 12 h. The solvent was evaporated *in vacuo* and the residue was purified by flash chromatography ($CHCl_3$/CH_3OH = 30/1) to afford compound **2** (0.44 g, 0.46 mmol, 87% in 2 steps) as a white solid. M.p.: 195 °C (dec.); R_f: 0.27 ($CHCl_3$/CH_3OH = 30/1); ^{1}H NMR: 10.24 (s, NH, 1 H), 9.65 (br s, NH, 1 H), 9.54 (br s, NH, 1 H), 8.74 (d, *J* = 2.6, ArH, 1 H), 8.60 (d, *J* = 2.5, ArH, 1 H), 8.17 (t, *J* = 5.2, NH, 1 H), 8.07 (d, *J* = 2.7, ArH, 1 H), 7.99 (d, *J* = 2.7, ArH, 1 H), 4.61 (d, *J* = 3.5, C*H*$_2$CONH, 2 H), 4.33 (t, *J* = 7.7, OCH_2, 2 H), 4.19 (t, *J* = 6.9, OCH_2, 2 H), 3.47 (q, *J* = 6.8, CONHC*H*$_2$, 2 H), 3.35 (s, C≡CH, 1 H), 2.48 (t, *J* = 7.4, C*H*$_2$CONH, 2 H), 1.93–1.57 (m, 10 H), 1.32–1.24 (m, 22 H), 1.16 (s, $(CH_3)_2$C*H*Si + $(CH_3)_2$CHSi, 21 H), 0.99 (d, *J* = 6.5, CH(C*H*$_3$)$_2$, 6 H), 0.91–0.85 (m, 12 H); ^{13}C NMR: (some signal overlappings of aliphatic carbon nuclei were observed) 172.5, 166.2, 165.2, 164.9, 155.3, 154.7, 135.1, 135.1, 131.0, 128.7, 126.9, 125.0, 122.7, 122.6, 119.1, 117.9, 102.7, 96.8, 82.7, 79.5, 75.0, 74.6, 45.4, 40.5, 39.2, 38.2, 37.4, 32.0, 31.9, 29.74, 29.69, 29.6, 29.51, 29.47, 29.4, 27.4, 25.7, 25.4, 25.1, 22.83, 22.80, 22.77, 18.9, 14.23, 14.20, 11.5; *m/z* (ESI) 978 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{57}H_{90}N_4O_6Si$ + Na^+: 977.6522, found: 977.6529; Anal. $C_{57}H_{90}N_4O_6Si$ requires C, 71.66; H, 9.49; N, 5.86%; found: C, 72.19; H, 9.29; N, 6.05%.

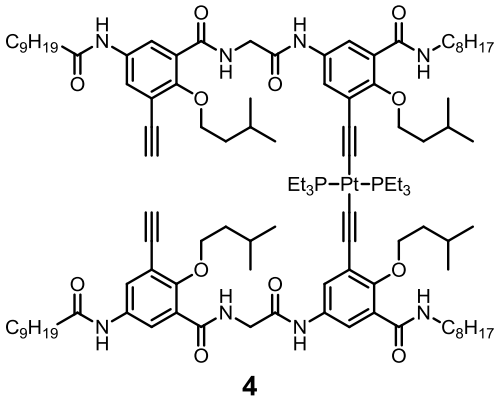
1.3 Synthesis of supramolecular ladder polymer **1**



3

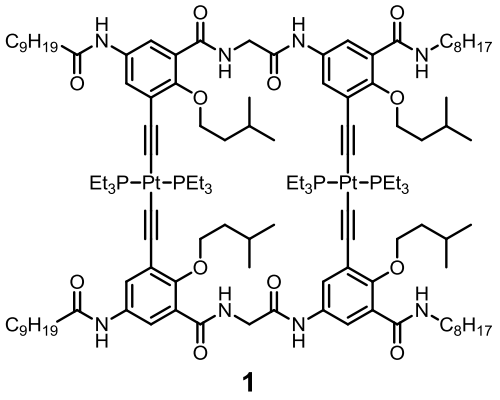
Compound 3. A mixture of compound **2** (0.40 g, 0.42 mmol), *trans*-$PtCl_2(PEt_3)_2$ (0.11 g, 0.21 mmol), disopropylamine (5 mL) in CH_2Cl_2 (30 mL) was frozen with liquid N_2 and degassed with N_2 (3 ×). The mixture was then stirred for 24 h at 25 °C. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography ($CHCl_3/CH_3OH$ = 30/1) to afford compound **3** (0.48 g, 0.21 mmol, 98%) as a pale yellow solid. M.p.: 278 °C (dec.); R_f: 0.5 ($CHCl_3/CH_3OH$ = 20/1); ^{1}H NMR: 10.10 (br s, NH, 2 H), 9.81 (br s, NH, 2 H), 9.51 (br s, NH, 2 H), 8.60 (s, ArH, 2 H), 8.58 (s, ArH, 2 H), 8.35 (br s, ArH, 2 H), 8.03 (br s, NH, 2 H), 7.84 (br s, ArH, 2 H), 4.62 (br s, CH_2CONH, 4 H), 4.31 (m, OCH_2, 8 H), 3.48 (m, CONHCH_2, 4 H), 2.49 (m, CH_2CONH, 4 H), 2.18–2.17 (m, P(C$H_2$$CH_3$)$_3$, 12 H), 1.87 (q, J = 7.2, OCH_2CH_2, 4 H), 1.72–1.61 (m, 16 H), 1.32–1.61 (m, 62 H), 1.15 (s, $(CH_3)_2$CHSi + (CH_3)$_2$CHSi, 42 H), 0.97–0.95 (m, 12 H), 0.89–0.85 (m, 24 H); ^{13}C NMR: (signal overlapping of acetylenic carbon nuclei was noted) 172.5, 165.9, 165.8, 165.0, 155.3, 153.1, 132.1, 134.7, 130.8, 128.2, 126.2, 125.3, 124.0, 122.8, 118.9, 115.7,[S4] 105.0,[S4] 102.8, 96.4, 74.8, 73.3, 45.4, 40.3, 39.1, 38.1, 37.3, 32.0, 31.9, 29.7, 29.63, 29.55, 29.5, 29.4, 29.3, 27.3, 25.6, 25.4, 25.3, 22.9, 22.8, 22.7, 18.8, 16.5 (pseudo quint, $J_{C\text{-}P}$ = 17.6), 14.2, 14.1, 11.5, 8.5 (pseudo t, $J_{C\text{-}P}$ = 11.3); ^{31}P NMR: 12.1 ($J_{Pt\text{-}P}$ = 2369); *m/z* (ESI) 2362 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{126}H_{208}N_8O_{12}P_2PtSi_2$ + Na^+: 2362.4491, found: 2362.4487.

[S4] Based on the ^{13}C NMR spectral data of other Pt-diacetylene compounds, the two acetylenic carbon signals are broad and sometimes difficult to identify, but they appear consistently at δ 115.7 and δ 105.0.



4

Compound 4. A solution of TBAF in THF (1 M, 0.4 mL) was added to a solution of compound **3** (0.28 g, 0.12 mmol) in THF (20 mL). The reaction mixture was stirred at 25 °C for 10 min. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography ($CHCl_3/CH_3OH$ = 20/1) to afford compound **4** (0.23 g, 0.11 mmol, 92%) as a pale yellow solid. M.p.: 272 °C (dec.); R_f: 0.29 ($CHCl_3/CH_3OH$ = 30/1); ^{1}H NMR: 10.08 (br s, NH, 2 H), 9.84 (br s, NH, 2 H), 9.49 (br s, NH, 2 H), 8.63 (br s, ArH, 2 H), 8.54 (br s, ArH, 2 H), 8.37 (br s, NH, 2 H), 8.07 (br s, ArH, 2 H), 7.83 (br s, ArH, 2 H), 4.62 (br s, C*H*$_2$CONH, 4 H), 4.26 (m, OCH_2, 8 H), 3.48 (br s, CONHC*H*$_2$, 4 H), 3.33 (s, C≡CH, 2 H), 2.48 (br s, C*H*$_2$CONH, 4 H), 2.16 (br s, P(C*H*$_2$CH$_3$)$_3$, 12 H), 1.89–1.26 (m, 82 H), 0.97 (m, 24 H), 0.89–0.85 (m, 12 H); ^{13}C NMR: 172.5, 166.0, 165.8, 164.8, 155.7, 153.2, 135.3, 134.7, 130.7, 128.1, 126.2, 125.3, 124.1, 123.3, 117.7, 115.9, 105.2, 82.5, 79.8, 74.8, 73.3, 45.4, 40.3, 39.2, 38.4, 37.3, 32.0, 31.9, 29.75, 29.68, 29.6, 29.52, 29.45, 29.4, 27.4, 25.7, 25.4, 25.1, 22.94, 22.88, 22.8, 16.5 (pseudo quint, $J_{C\text{-}P}$ = 17.5), 14.22, 14.19, 8.6; ^{31}P NMR: 12.2 ($J_{Pt\text{-}P}$ = 2369); *m/z* (ESI) 2049 (M + Na^+, 50%), 2027 (M^+, 100%); HRMS (ESI) calcd for $C_{108}H_{168}N_8O_{12}P_2Pt^+$: 2027.1927, found: 2027.1976.



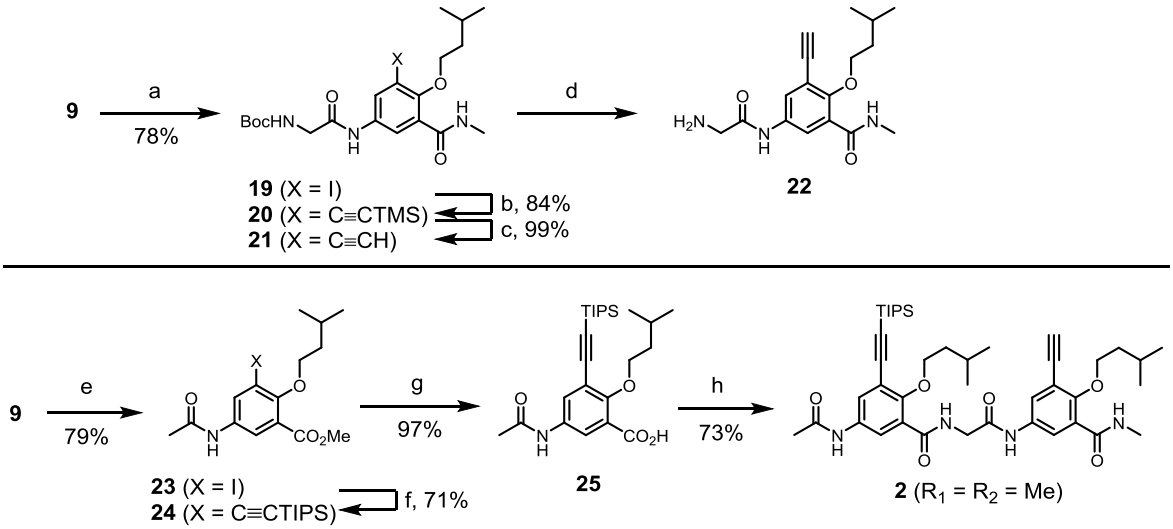
1

Compound 1. A solution of compound **4** (0.12 g, 59.2 μmol), CuI (11 mg, 52 μmol) and diisopropylamine (5 mL) in CH_2Cl_2 (60 mL) was frozen with liquid N_2 and degassed with N_2

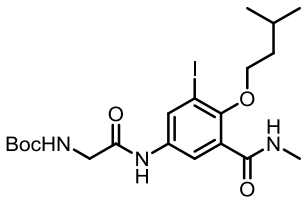
(3 ×). The mixture was then warmed to 25 °C. A solution of *trans*-$PtCl_2(PEt_3)_2$ (30 mg, 59.2 μmol) in CH_2Cl_2 (20 mL) was added dropwise over a period of 1 h to the mixture and stirred at 25 °C for 2 d. The solvent was evaporated *in vacuo*. The residue was taken up with $CHCl_3/CH_3OH$ (30/1) and filtered through a short pad of silica gel. The filtrate was then concentrated and the crude product was isolated by precipitation in methanol. The crude product was further purified by washing with THF (20 mL × 3) to afford the target metallomacrocycle **1** (90 mg, 36.7 μmol, 62%) as a pale yellow solid. M.p.: 382 °C; R_f: 0.33 ($CHCl_3/CH_3OH$ = 20/1); ^{1}H NMR (4% $CD_3OH/CDCl_3$):[S5] 10.16 (br s, NH, 2 H), 9.78 (br s, NH, 2 H), 9.59 (br s, NH, 2 H), 8.70 (s, ArH, 2 H), 8.37 (br s, NH, 2 H), 8.28 (s, ArH, 2 H), 7.79 (br s, ArH, 4 H), 4.58 (br s, C*H*$_2$CONH, 4 H), 4.38 (br s, OCH_2, 4 H), 4.31 (br s, OCH_2, 4 H), 3.48 (br s, CONHC*H*$_2$, 4 H), 2.53 (br s, C*H*$_2$CONH, 4 H), 2.17 (br s, P(C*H*$_2$CH$_3$)$_3$, 24 H), 1.86–1.16 (m, 100 H), 0.98–0.86 (m, 36 H); ^{13}C NMR (4% $CD_3OH/CDCl_3$): 172.6, 166.2, 165.9, 165.7, 154.8, 152.8, 135.0, 134.3, 129.4, 127.8, 126.0, 124.8, 123.9, 115.6, 105.2, 73.4, 73.2, 45.3, 40.2, 39.1, 38.1, 37.4, 32.0, 31.9, 29.7, 29.6, 29.6, 29.4, 29.4, 29.3, 27.3, 25.4, 23.0, 22.9, 22.7, 16.7 (pseudo quint, J_{P-C} = 17.5), 16.4 (pseudo quint, J_{P-C} = 17.6), 14.13, 14.11, 8.5 (pseudo t, J_{P-C} = 11.3); ^{31}P NMR (4% $CD_3OH/CDCl_3$): 12.5 (J_{Pt-P} = 2372), 11.9 (J_{Pt-P} = 2363); *m/z* (ESI) 2479 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{120}H_{196}N_8O_{12}P_4Pt_2$ + Na^+: 2479.3136, found: 2479.3133. Anal. $C_{120}H_{196}N_8O_{12}P_4Pt_2$ requires C, 58.66; H, 8.04; N, 4.56; P, 5.04%; found: C, 57.98; H, 8.34; N, 4.50; P 4.99%.

[S5] Significant broadening of ^{13}C signals, especially the acetylenic ones, was noted. As a result, some signals could not be identified with certainty and were not reported here.

1.4 Synthesis of DADA quadruple H-bonding analog **2** ($R_1 = R_2 = Me$) for X-ray crystallographic analysis

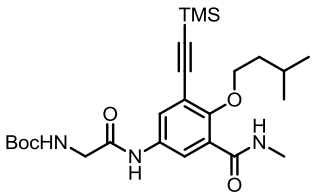


Scheme S2. Reagent and conditions: (a) EDCI, HOBt, CH_2Cl_2, 30 min, then CH_3NH_2•HCl, Et_3N, CH_2Cl_2, 12 h; (b) TMSC≡CH, $PdCl_2(PPh_3)_2$, cat. CuI, Et_3N, THF, 50 °C, 12 h; (c) TBAF, THF, 10 min; (d) TFA, CH_2Cl_2, 1 h; (e) Ac_2O, CH_2Cl_2, 3 h; (f) TIPSC≡CH, $PdCl_2(PPh_3)_2$, cat. CuI, Et_3N, THF, 50 °C, 12 h; (g) KOH, THF, H_2O, 24 h; (h) EDCI, HOBt, CH_2Cl_2, 30 min, then compound **22**, CH_2Cl_2, 12 h.



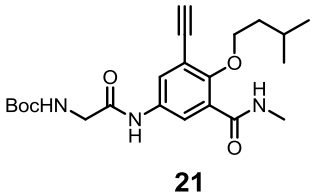
19

Compound 19. EDCI (0.35 g, 1.17 mmol) and HOBt (0.16 g, 1.17 mmol) were added to a solution of compound **9** (0.54 g, 1.07 mmol) in CH_2Cl_2 (30 mL) and stirred at 25 °C for 30 min. After 30 min, Et_3N (1 mL) and methylammonium chloride (0.22 g, 3.20 mmol) were added and the reaction mixture was stirred at 25 °C for 12 h. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography ($CHCl_3/CH_3OH/Et_3N$ = 300/10/1) to afford compound **19** (0.55 g, 0.83 mmol, 78%) as a white solid. M.p.: 114–115; R_f: 0.30 ($CHCl_3/CH_3OH/Et_3N$ = 300/10/1); ^{1}H NMR: 9.28 (s, NH, 1 H), 8.50 (s, ArH, 1 H), 7.82 (m, NH, 1 H), 7.79 (d, J = 2.5, ArH, 1 H), 5.66 (br s, N*H*Boc, 1 H), 3.99 (br s, CH_2NHBoc, 2 H), 3.85 (t, J = 6.8, OCH_2, 2 H), 3.00 (d, J = 4.8, CONHCH_3, 3 H), 1.85–1.68 (m, 3 H), 1.42 (s, $C(CH_3)_3$, 9 H), 0.96 (d, J = 6.5, $CH(CH_3)_2$, 6 H); ^{13}C NMR: 168.4, 165.4, 156.4, 152.6, 135.7, 133.9, 127.3, 122.7, 93.2, 80.2, 74.4, 44.9, 39.0, 28.4, 26.9, 24.9, 22.8; *m/z* (ESI) 542 ($M + Na^+$, 100%); HRMS (ESI) calcd for $C_{20}H_{30}IN_3O_5 + Na^+$: 542.1122, found: 542.1127.



20

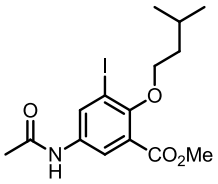
Compound 20. A mixture of compound **19** (0.36 g, 0.69 mmol), trimethylsilylacetylene (1.00 mL, 6.93 mmol), CuI (13 mg, 69.3 μmol), $Pd(PPh_3)_2Cl_2$ (49 mg, 69.3 μmol) and Et_3N (0.5 mL) in dry THF (20 mL) was frozen in a sealed tube with liquid N_2 and degassed with N_2 (3 ×). The mixture was stirred at 50 °C for 12 h, filtered through a short pad of Celite and washed with Et_2O (20 mL). The filtrate was concentrated *in vacuo* and the residue purified by flash chromatography ($CHCl_3/Et_3N$ = 100/1 gradient to $CHCl_3/CH_3OH/Et_3N$ = 200/100/1) to give a solid which was further purified by recrystallization from hexane to afford compound **20** (0.28 g, 0.58 mmol, 84%) as an off-white solid. M.p.: 170–171 °C (dec.); R_f: 0.37 ($CHCl_3/CH_3OH/Et_3N$ = 200/10/1); ^{1}H NMR: 9.32 (br s, NH, 1 H), 8.26 (br s, ArH, 1 H), 8.09 (m, NH, 1 H), 7.84 (d, *J* = 2.2, ArH, 1 H), 5.62 (t, *J* = 5.1, N*H*Boc, 1 H), 4.13 (t, *J* = 6.8, OCH_2, 2 H), 4.00 (br s, C*H*$_2$NHBoc, 2 H), 2.99 (d, *J* = 4.7, CONHC*H*$_3$, 3 H), 1.83–1.66 (m, 3 H), 1.41 (s, $C(CH_3)_3$, 9 H), 0.95 (d, *J* = 6.5, $CH(CH_3)_2$, 6 H), 0.22 (s, $(CH_3)_3Si$, 9 H); ^{13}C NMR: 168.2, 165.4, 156.2, 154.8, 134.2, 128.9, 126.4, 122.8, 118.6, 100.3, 100.1, 80.0, 74.1, 44.8, 39.0, 28.4, 26.8, 25.1, 22.7, -0.1; *m/z* (ESI) 512 ($M + Na^+$, 100%); HRMS (ESI) calcd for $C_{25}H_{39}N_3O_5Si + Na^+$: 512.2551, found: 512.2553.



21

Compound 21. A solution of TBAF in THF (1 M, 0.6 mL) was added to a solution of **20** (0.28 g, 0.57 mmol) in THF (20 mL). The reaction mixture was stirred at 25 °C for 10 min. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography ($CHCl_3/CH_3OH/Et_3N$ = 300/100/1) to afford compound **21** (0.24 g, 0.56 mmol, 99%) as a pale yellow solid. M.p.: 162–163 °C; R_f: 0.33 ($CHCl_3/CH_3OH/Et_3N$ = 300/100/1); ^{1}H NMR: 8.86 (br s, NH, 1 H), 8.28 (d, *J* = 2.7, ArH, 1 H), 8.05 (m, NH, 1 H), 7.87 (d, *J* = 2.8, ArH, 1 H), 5.42 (br s, N*H*Boc, 1 H), 4.15 (t, *J* = 6.8, OCH_2, 2 H), 3.99 (d, *J* = 5.3, C*H*$_2$NHBoc, 2 H), 3.32 (s, C≡CH, 1 H), 3.02 (d, *J* = 4.9, CONHC*H*$_3$, 3 H), 1.87–1.67 (m, 3 H), 1.46 (s, $C(CH_3)_3$, 9 H),

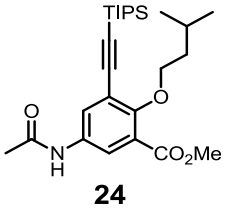
0.97 (d, J = 6.6, CH(CH_3)$_2$, 6 H); ^{13}C NMR: 168.3, 165.4, 156.3, 155.0, 134.3, 128.9, 126.7, 123.1, 117.5, 82.6, 80.0, 79.3, 74.2, 44.8, 39.0, 28.4, 26.8, 24.9, 22.6; *m/z* (ESI) 440 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{22}H_{31}N_3O_5$ + Na^+: 440.2156, found: 440.2158.



23

Compound 23. Compound **8** (1.29 g, 3.28 mmol) was added to a solution of $Na_2S_2O_4$ (5.71 g, 32.8 mmol) in THF (50 mL) and H_2O (50 mL). The reaction mixture was stirred at 25 °C for 2 h. The solvent was evaporated *in vacuo* and the residue extracted with EtOAc (250 mL). The combined organic solvents were washed with brine, dried ($MgSO_4$), and filtered. The solvent was evaporated and the crude amine **9** was used in the next step without further purification.

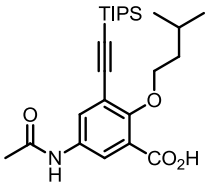
Acetic anhydride (0.44 g, 4.27 mmol) was added to the solution of the amine **9** in CH_2Cl_2 (30 mL). The reaction mixture was stirred at 25 °C for 3 h. The solvent was evaporated *in vacuo* and the residue purified by flash column chromatography (EtOAc) to afford compound **23** as a white solid (1.05 g, 2.59 mmol, 79% in 2 steps). M.p.: 120–121 °C; R_f: 0.66 (EtOAc); ^{1}H NMR: 8.80 (s, NH, 1 H), 8.14 (d, J = 2.2. ArH, 1 H), 7.85 (d, J = 2.3. ArH, 1 H), 3.86 (t, J = 6.6, OCH_2, 2 H), 3.81 (s, CO_2CH_3, 3 H), 2.14 (s, CH_3CONH, 3 H), 1.86–1.75 (m, CH(CH_3)$_2$, 1 H), 1.68 (q, J = 6.6, OCH_2CH_2, 2 H), 0.92 (d, J = 6.6, CH(CH_3)$_2$, 6 H); ^{13}C NMR: 169.5, 165.5, 154.6, 135.0, 134.8, 125.0, 123.3, 94.2, 74.0, 52.5, 38.9, 24.8, 24.3, 22.8; *m/z* (ESI) 428 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{15}H_{20}INO_4$ + Na^+: 428.0329, found: 428.0330.



24

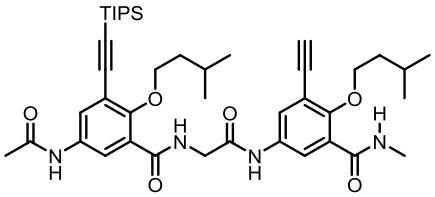
Compound 24. A mixture of compound **23** (0.65 g, 1.60 mmol), triisopropylsilylacetylene (1.10 mL, 4.81 mmol), CuI (31 mg, 0.16 mmol), Pd(PPh_3)$_2Cl_2$ (0.11 g, 0.16 mmol) and Et_3N (5 mL) in dry THF (30 mL) was frozen in a sealed tube with liquid N_2 and degassed with N_2 (3 ×). The mixture was stirred at 50 °C for 12 h. The reaction mixture was filtered through a short pad of Celite and then washed with Et_2O (20 mL). The filtrate was concentrated *in vacuo* and the residue purified by flash chromatography (hexane/$CHCl_3$ = 1/3) to afford compound **24**

(0.52 g, 1.14 mmol, 71%) as a yellow oil. R_f: 0.25 (hexane/$CHCl_3$ = 1/3); ^{1}H NMR: 7.80–7.77 (m, ArH, 2 H), 7.12 (br s, NH, 1 H), 4.14 (t, *J* = 7.0, OCH_2, 2 H), 3.89 (s, CO_2CH_3, 3 H), 2.16 (s, C*H*$_3$CONH, 3 H), 1.80–1.69 (m, 3 H), 1.13 (s, $(CH_3)_2CHSi$ + $(CH_3)_2CHSi$, 21 H), 0.93 (d, *J* = 6.2, $CH(CH_3)_2$, 6 H); ^{13}C NMR: 169.3, 166.2, 156.4, 133.5, 129.6, 125.6, 123.0, 119.8, 102.2, 96.4, 74.0, 52.3, 38.8, 25.0, 24.1, 22.7, 18.7, 11.3; *m/z* (ESI) 482 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{26}H_{41}NO_4Si$ + Na^+: 482.2697, found: 482.2697.



25

Compound 25. A mixture of compound **24** (0.50 g, 1.09 mmol) in THF (30 mL) and aqueous KOH solution (2.5 M, 10 mL) was stirred at 25 °C for 12 h. The reaction mixture was concentrated *in vacuo* and acidified with saturated NH_4Cl solution (50 mL). The mixture was then extracted with EtOAc (3 × 50 mL) and the combined extracts washed with brine, dried ($MgSO_4$), filtered and evaporated *in vacuo* to give compound **25** (0.47 g, 1.06 mmol, 97%) as a pale yellow solid. M.p.: 188–189 °C; R_f: 0.1 (hexane/$CHCl_3$ = 1/3); ^{1}H NMR: 11.51 (br s, CO_2H, 1 H), 9.04 (s, NH, 1 H), 8.50 (d, *J* = 1.6, ArH, 1 H), 7.99 (s, ArH, 1 H), 4.46 (t, *J* = 6.8, OCH_2, 2 H), 2.24 (s, C*H*$_3$CONH, 3 H), 1.75–1.72 (m, 3 H), 1.11 (s, $(CH_3)_2CHSi$ + $(CH_3)_2CHSi$, 21 H), 0.93 (d, *J* = 6.0, $CH(CH_3)_2$, 6 H); ^{13}C NMR: 169.8, 165.9, 154.9, 135.5, 131.4, 123.5, 121.8, 118.2, 101.4, 98.8, 75.5, 38.5, 25.2, 24.3, 22.6, 18.7, 11.3; *m/z* (ESI) 468 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{25}H_{39}NO_4Si$ + Na^+: 468.2541, found: 468.2546.

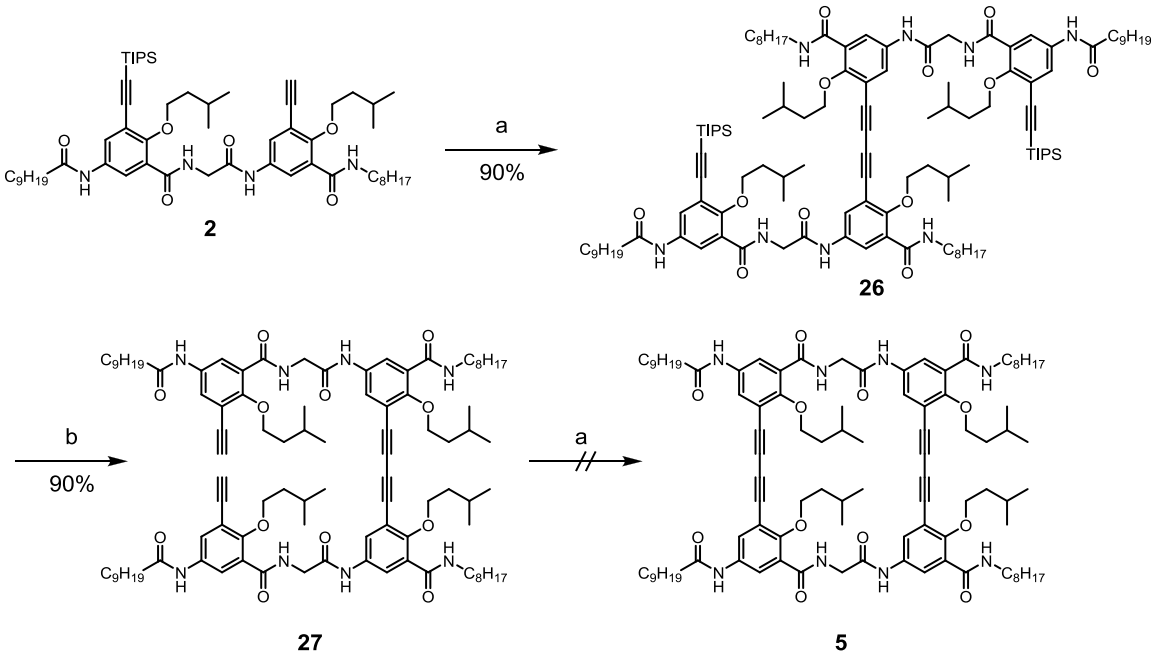


2 (R_1 = R_2 = Me)

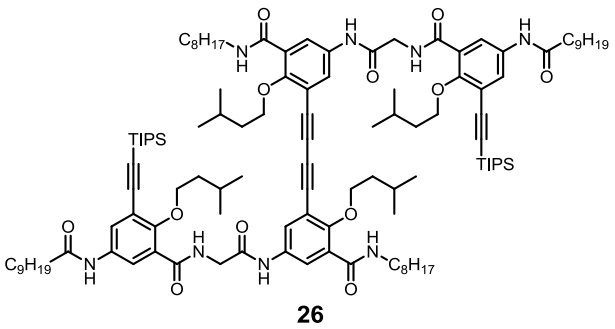
Compound 2 (R_1 = R_2 = Me)**.** A mixture of trifluoroacetic acid (3 mL) and compound **21** (0.26 g, 0.63 mmol) in CH_2Cl_2 (30 mL) was stirred at 25 °C for 1 h. The reaction mixture was then neutralized with saturated Na_2CO_3 solution, extracted with CH_2Cl_2 (3 × 50 mL) and the combined extracts were washed with brine, dried ($MgSO_4$), filtered and evaporated *in vacuo* to give crude amine **22** which was used in the next step without further purification.

EDCI (0.20 g, 0.69 mmol) and HOBt (92.6 g, 0.69 mmol) were added to a solution of acid **25** (0.28 g, 0.63 mmol) in CH_2Cl_2 (30 mL). After 30 min, a solution of the amine **22** in CH_2Cl_2 (10 mL) was then added and the reaction mixture stirred at 25 °C for 12 h. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography ($CHCl_3/CH_3OH$ = 20/1) to give a solid which was further purified by recrystallization from methanol to afford compound **26** (0.34 g, 0.46 mmol, 73% in 2 steps) as a white solid. M.p.: 247–248 °C (dec.); R_f: 0.23 ($CHCl_3/CH_3OH$ = 20/1); ^{1}H NMR: 10.24 (s, NH, 1 H), 9.78 (s, NH, 1 H), 9.56 (s, NH, 1 H), 8.74 (d, *J* = 2.3, ArH, 1 H), 8.57 (d, *J* = 2.2, ArH, 1 H), 8.22 (m, NH, 1 H), 8.06 (d, *J* = 2.4, ArH, 1 H), 7.99 (s, ArH, 1 H), 4.62 (d, *J* = 3.0, C*H*$_2$CONH, 2 H), 4.34 (t, *J* = 7.5, OCH_2, 2 H), 4.19 (t, *J* = 6.6, OCH_2, 2 H), 3.34 (s, C≡CH, 1 H), 3.04 (d, *J* = 4.7, CONHC*H*$_3$, 3 H), 2.27 (s, C*H*$_3$CONH, 3 H), 1.93–1.61 (m, 6 H), 1.16 (s, $(CH_3)_2$C*H*Si + $(CH_3)_2$CHSi, 21 H), 0.99 (d, *J* = 6.5, CH(C*H*$_3$)$_2$, 6 H), 0.91 (d, *J* = 6.6, CH(C*H*$_3$)$_2$, 6 H); ^{13}C NMR: 169.4, 166.2, 165.8, 165.0, 155.3, 154.8, 135.1, 135.0, 131.0, 128.7, 126.6, 125.0, 122.6, 122.5, 119.1, 117.9, 102.8, 97.0, 82.7, 79.4, 75.0, 74.5, 45.4, 39.1, 38.2, 27.1, 25.4, 25.1, 24.5, 22.8, 22.7, 18.9, 11.5; *m/z* (ESI) 767 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{42}H_{60}N_4O_6Si$ + Na^+: 767.4174, found: 767.4178.

1.5 Attempted synthesis of diacetylene-linked macrocycle **5**



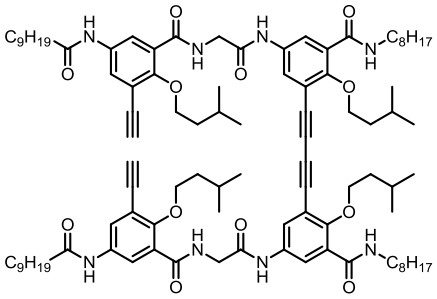
Scheme S3. Reagent and conditions: (a) TMEDA, CuCl, CH_2Cl_2, O_2 (1 atm), 24 h; (b) TBAF, THF, 10 min.



Compound 26. A mixture of compound **2** (0.21 g, 0.22 mmol), CuCl (0.11 g, 1.10 mmol) and tetramethylethylenediamine (TMEDA) (0.16 mL, 1.10 mmol) were stirred in CH_2Cl_2 (10 mL) under O_2 (1 atm) at 25 °C for 24 h. The solvent was evaporated *in vacuo* and the residue subjected to flash column chromatography ($CHCl_3/CH_3OH$ = 20/1) to afford compound **26** (0.19 g, 98.9 μmol, 90%) as a white solid. M.p.: 270 °C (dec.); R_f: 0.33 ($CHCl_3/CH_3OH$ = 20/1); ^{1}H NMR (10% CD_3OH in $CDCl_3$):[S6] 10.12 (br s, NH, 2 H), 9.52 (br s, NH, 2 H), 9.20 (br s, NH, 2 H), 8.53 (br s, ArH, 2 H), 8.43 (br s, ArH, 2 H), 8.15 (br s, NH, 2 H), 7.90 (br s, ArH, 2 H), 7.82 (br s, ArH, 2 H), 4.43–4.24 (m, C*H*$_2$CONH + OCH$_2$, 12 H), 2.41 (br s, C*H*$_2$CONH, 4 H), 1.83–0.90 (m, 142 H); ^{13}C NMR (10% $CD_3OH/CDCl_3$, 35 °C): 173.1, 166.9, 165.7, 164.9, 155.8, 155.2, 134.9, 134.9, 130.4, 128.8, 127.3, 125.6, 123.5, 122.6, 119.0, 117.3,

[S6] ^{1}H-NMR signal of CONHC*H*$_2$ (4 H) was found to merge with that of residual H_2O.

102.7, 97.1, 78.7, 78.6, 75.0, 74.9, 44.7, 40.4, 39.2, 38.5, 37.4, 32.0, 31.9, 29.6, 29.49, 29.46, 29.4, 29.3, 27.3, 25.8, 25.4, 25.2, 22.8, 22.7, 18.8, 14.1, 11.5; *m/z* (ESI) 1931 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{114}H_{178}N_8O_{12}Si_2$ + Na^+: 1931.3025, found: 1931.3028.



27

Compound 27. A solution of TBAF in THF (1 M, 0.15 mL) was added to a solution of **26** (0.26 g, 0.14 mmol) in THF (20 mL). The reaction mixture was stirred at 25 °C for 10 min. The solvent was evaporated *in vacuo* and the residue purified by flash chromatography ($CHCl_3$/CH_3OH = 20/1) to afford compound **27** (0.20 g, 0.12 mmol, 90%) as a white solid. M.p.: >350 °C (dec.); R_f: 0.43 ($CHCl_3$/CH_3OH = 20/1); ^{1}H NMR (10% CD_3OH in $CDCl_3$, 35 °C): 9.99 (s, NH, 2 H), 9.37 (s, NH, 2 H), 9.12 (s, NH, 2 H), 8.50 (d, *J* = 2.2, ArH, 2 H), 8.40 (s, ArH, 2 H), 8.08 (t, *J* = 5.0, NH, 2 H), 7.92 (d, *J* = 2.7, ArH, 2 H), 7.86 (d, *J* = 2.6, ArH, 2 H), 4.43 (d, *J* = 4.1, C*H*$_2$CONH, 4 H), 4.30–4.23 (m, OCH_2, 8 H), 3.47 (q, *J* = 6.7, CONHC*H*$_2$, 4 H), 3.38 (s, C≡CH, 2 H), 2.40 (t, *J* = 7.4, C*H*$_2$CONH, 4 H), 1.92–1.60 (m, 20 H), 1.40–1.27 (m, 44 H), 1.02 (d, *J* = 6.5, CH(C*H*$_3$)$_2$, 12 H), 0.97 (d, *J* = 6.2, CH(C*H*$_3$)$_2$, 12 H), 0.90–0.86 (m, CH_3, 12 H); ^{13}C NMR (10% CD_3OH in $CDCl_3$, 35 °C): 173.1, 167.0, 165.6, 165.0, 155.8, 155.7, 135.0, 134.9, 130.1, 128.9, 127.3, 125.8, 123.5, 123.0, 117.8, 117.3, 82.9, 79.6, 78.7, 75.0, 74.8, 44.7, 40.4, 39.3, 38.8, 37.4, 32.0, 31.9, 29.62, 29.59, 29.50, 29.47, 29.4, 29.3, 27.3, 25.8, 25.25, 25.17, 22.8, 14.09, 14.07; *m/z* (ESI) 1619 (M + Na^+, 100%); HRMS (ESI) calcd for $C_{96}H_{138}N_8O_{12}$ + Na^+: 1619.0359, found: 1619.0364.

Attempted Synthesis of Compound 5. A mixture of CuCl (31 mg, 0.31 mmol) and tetramethylethylenediamine (TMEDA) (47 μL, 0.31 mmol) were stirred in CH_2Cl_2 (50 mL) under O_2 (1 atm). A solution of compound **27** (0.10 g, 62.6 μmol) in CH_2Cl_2 (20 mL) was added dropwise over a period of 1 h and the mixture was stirred at 25 °C for 2 d. The solvent was evaporated *in vacuo* and the residue subjected to flash column chromatography ($CHCl_3$/CH_3OH = 20/1) to afford a solid. The size exclusion chromatographic analysis revealed that the solid was a complex mixture of oligomers.

2. ^{1}H-, ^{31}P-NMR characterization and 2D NMR experiments of compounds **1**, **2**, **3** and **4**

2.1. ^{1}H-NMR spectra of supramolecular ladder polymer **1** in the presence of different amount of CD_3OH in $CDCl_3$

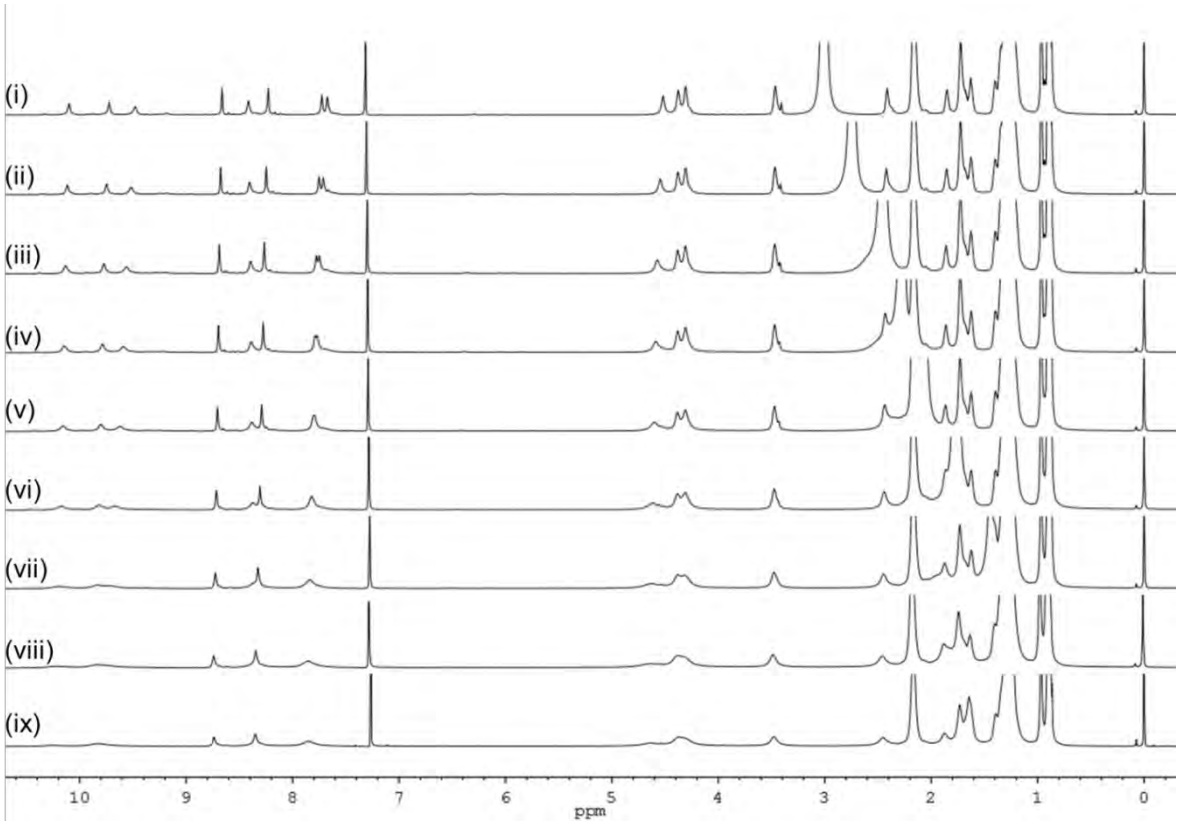


Figure S1. Stacked ^{1}H-NMR spectra (10 mM, 700 MHz) of supramolecular ladder polymer **1** in different percentage of $CD_3OH/CDCl_3$ (i) 5%, (ii) 4%, (iii) 3%, (iv) 2.5%, (v) 2%, (vi) 1.5%, (vii) 1%, (viii) 0.5% and (ix) pure $CDCl_3$.

2.2. ^{31}P-NMR spectra of supramolecular polymer **3**, **4** and supramolecular ladder polymer **1**

PPh_3 was used as external standard.

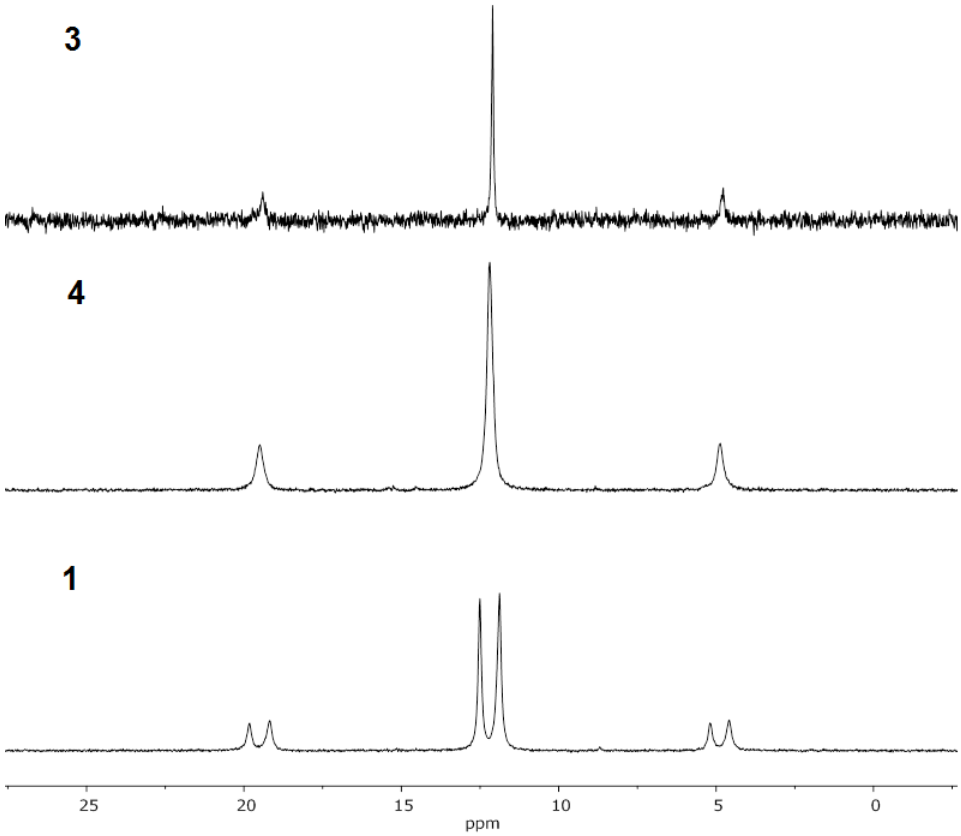


Figure S2. ^{31}P-NMR spectrum of (162 MHz) of (top) supramolecular polymer **3** ($CDCl_3$), (middle) supramolecular polymer **4** ($CDCl_3$) and (bottom) supramolecular ladder polymer **1** (4% $CD_3OH/CDCl_3$).

2.3. 2D ROESY spectra of dimer **2**, supramolecular ladder polymer **1** and supramolecular polymer **3**

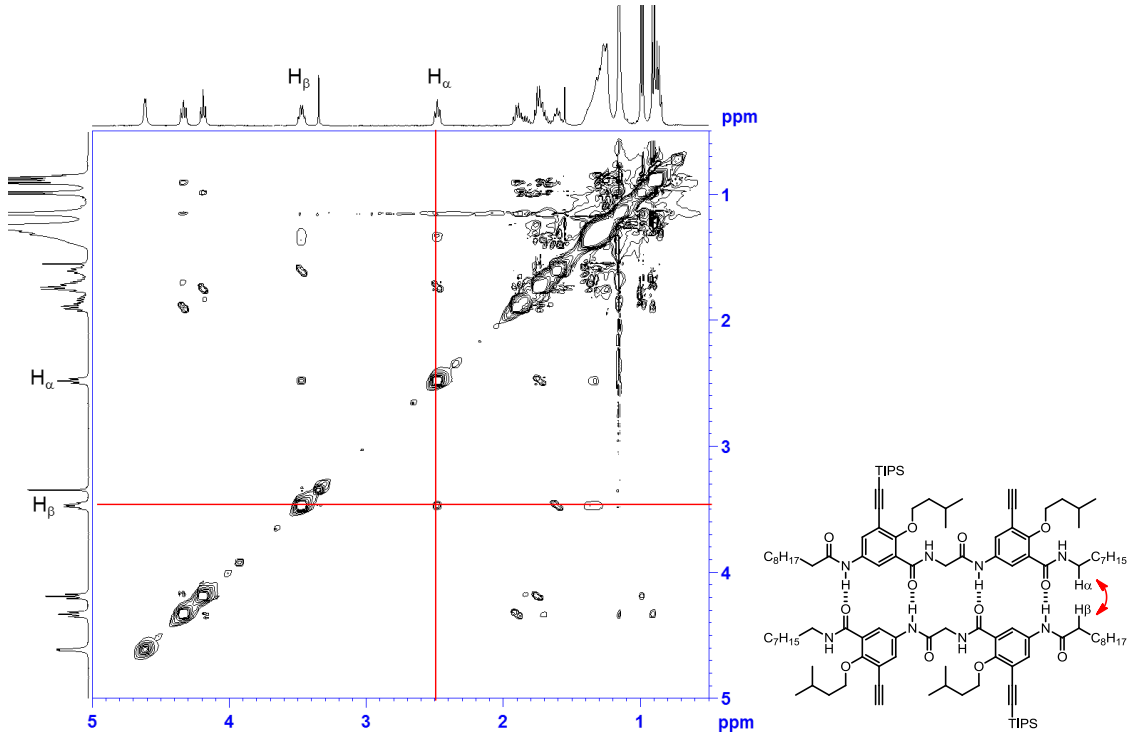


Figure S3. Partial ROESY spectrum (400 MHz, 10 mM, $CDCl_3$) of dimer **2** (red arrow indicating observed intermolecular NOE contact).

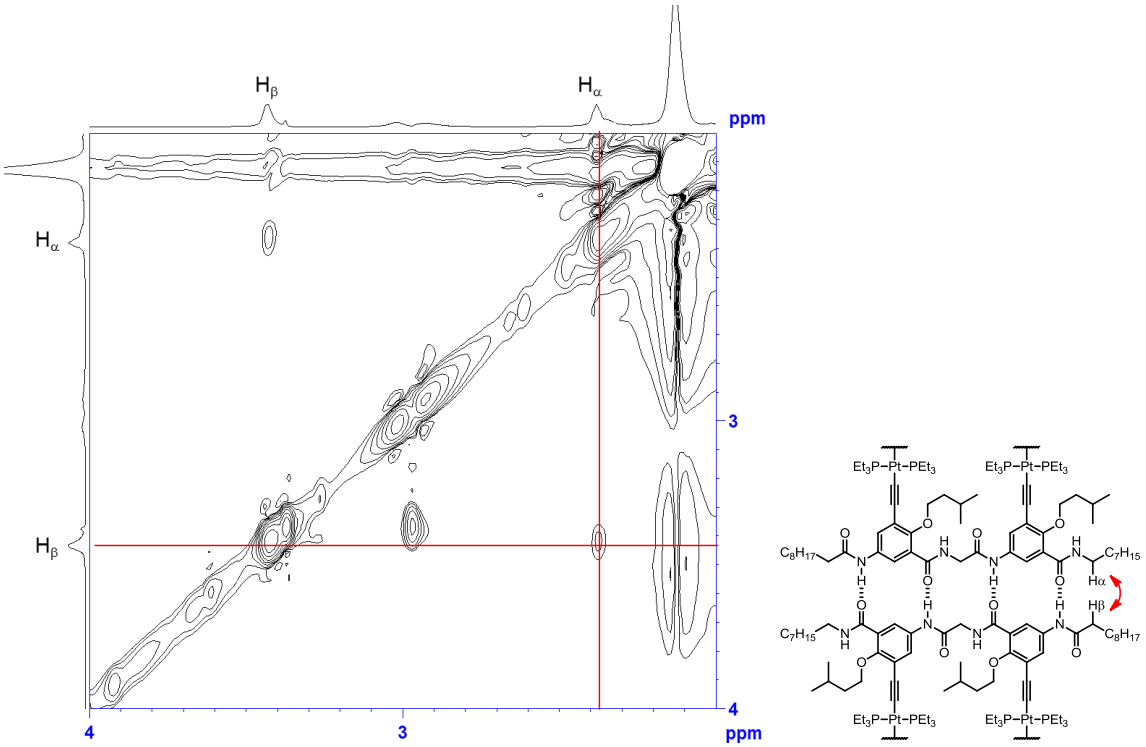


Figure S4. Partial ROESY spectrum with water suppression (700 MHz, 7 mM, 2% $CD_3OH/CDCl_3$) of supramolecular ladder polymer **1** (red arrow indicating observed intermolecular NOE contact).

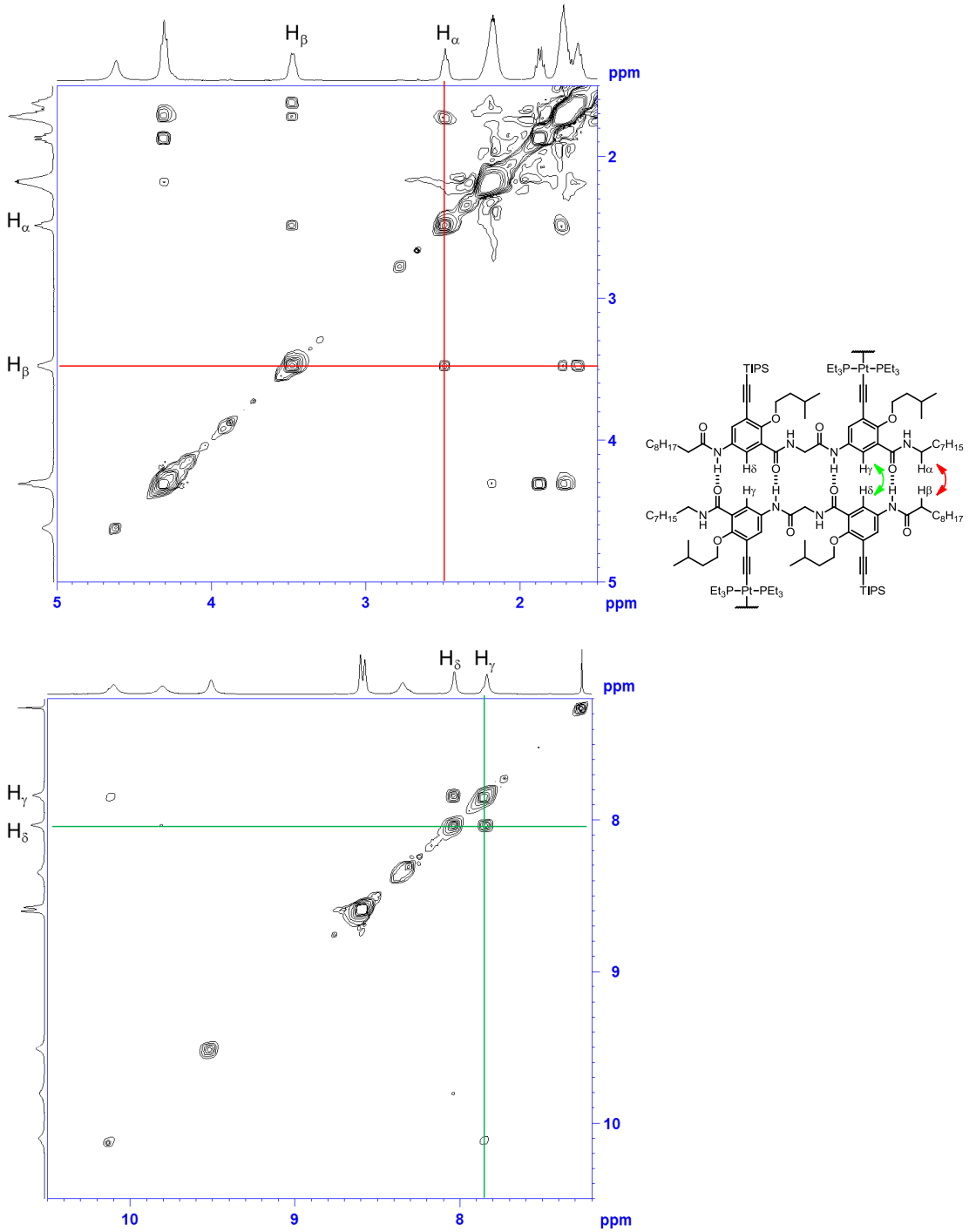


Figure S5. Partial ROESY spectrum (400 MHz, 50 mM, $CDCl_3$) of supramolecular polymer **3** (red and green arrows indicating observed intermolecular NOE contacts).

3. Determination of dimerization K_{dim} and association constants K_{ass}

3.1. Association models

The dimerization model reported by Moore[7] was used to determination the K_{dim} value of compound **2**. The value was obtained by curve fitting using a commercial program.

$$A + A \underset{}{\overset{K_d}{\rightleftharpoons}} A_2$$

$$K_{dim} = \frac{[A_2]}{[A]^2}$$

$$\delta_{obs} = \delta_d - \frac{-1 + \sqrt{1 + 8K_{dim}c_t}}{4K_{dim}c_t}(\delta_d - \delta_m)$$

where δ_{obs} is the observed chemical shift of a NMR signal,

δ_m is the chemical shift of monomer A,

δ_d is the chemical shift of dimer A_2

The isodesmic model reported by Moore[S7] was used to determination the K_{ass} values of compounds **1** and **3**. The values were obtained by curve fitting using a commercial program.

$$A_{j-1} + A \underset{}{\overset{K_j}{\rightleftharpoons}} A_j \quad \text{and} \quad K_j = \frac{[A_j]}{[A][A_{j-1}]} = \frac{[A_j]}{K_2 K_3 \cdots K_{j-1}[A]^j} \quad \text{for } j \geq 2$$

$$K = K_j \quad \text{for } j \geq 2$$

$$\delta_{obs} = \frac{[A]}{c_t}\delta_m + \frac{c_t - [A]}{c_t}\delta_{agg} = \delta_{agg} - \frac{[A]}{c_t}(\delta_{agg} - \delta_m)$$

$$= \delta_{agg} - \frac{2Kc_t + 1 - \sqrt{1 + 4Kc_t}}{2K^2 c_t^{\,2}}(\delta_{agg} - \delta_m)$$

where δ_{obs} is the observed chemical shift of a NMR signal,

δ_m is the chemical shift of monomer A,

δ_{agg} is the chemical shift of the aggregated species

[S7] D. Zhao, J. S. Moore, *Org. Biomol. Chem.* **2003**, *1*, 3471.

3.2. K_{dim} of dimer **2** in $CDCl_3$

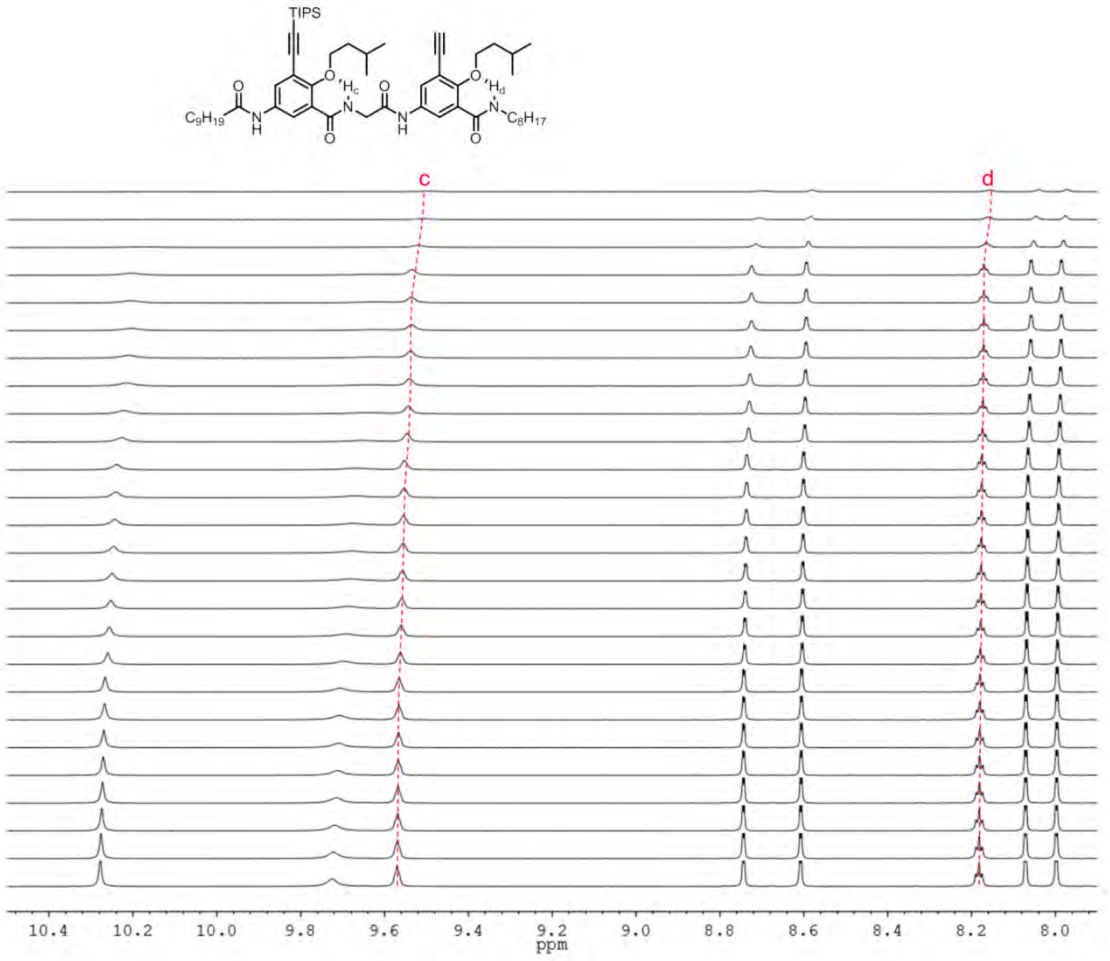


Figure S6. Stacked partial ^{1}H NMR spectra (700 MHz, $CDCl_3$) of DADA quadruple H-bonding array **2** from 0.3 to 50 mM (from top to bottom).

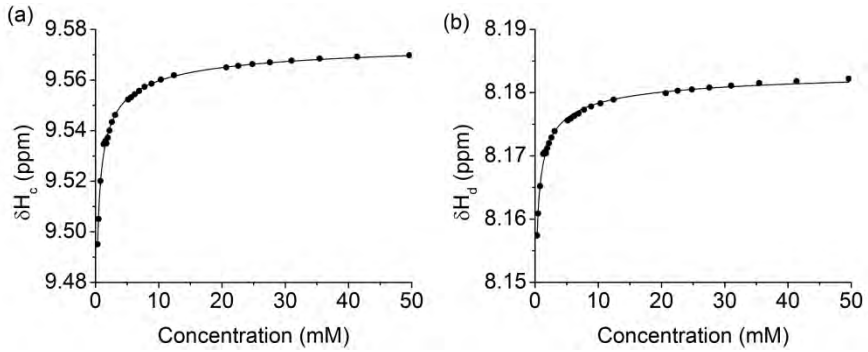


Figure S7. Concentration dependent ^{1}H-NMR data of DADA quadruple H-bonding array **2**: (a) H_c; (b) H_d.

Table S1. K_{dim} value of DADA quadruple H-bonding array **2**.

Signal	K_{dim} (M^{-1})	δ_m (ppm)	δ_d (ppm)	Adjusted r^2
H_c	6000 ± 2000	9.37 ± 0.02	9.5782 ± 0.0006	0.9969
H_d	4000 ± 1000	8.125 ± 0.006	8.1846 ± 0.0003	0.9955
	5000 ± 2000 (average)			

3.3. K_{dim} of dimer **2** in 2% $CD_3OH/CDCl_3$

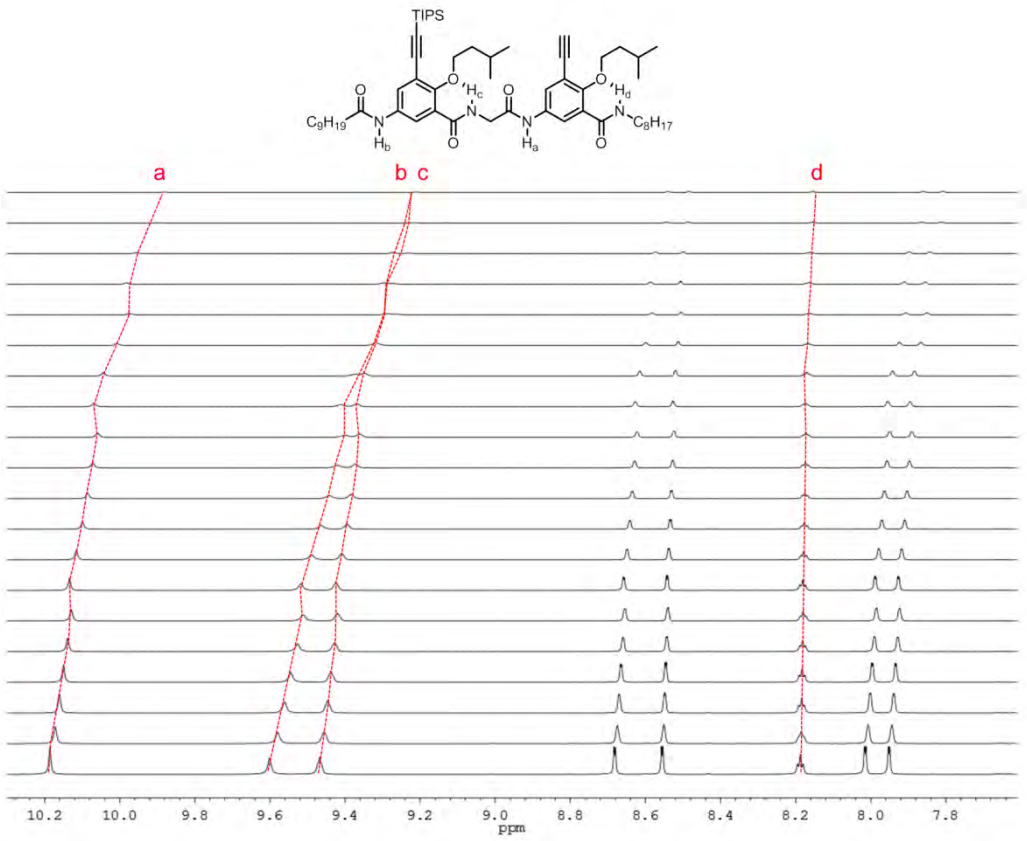


Figure S8. Stacked partial ^{1}H NMR spectra (700 MHz, 2% $CD_3OH/CDCl_3$) of DADA quadruple H-bonding array **2** from 0.3 to 20 mM (from top to bottom).

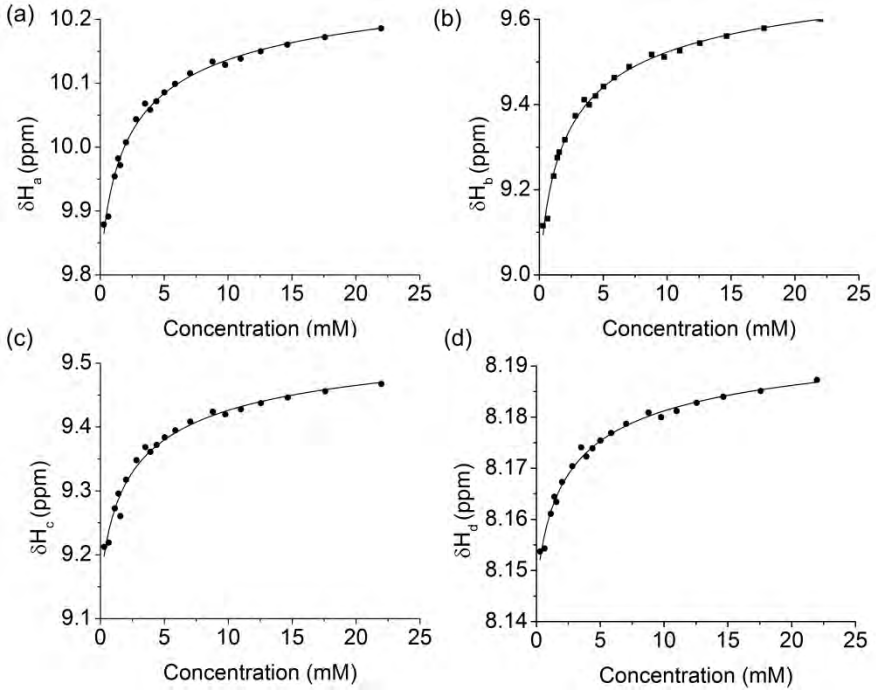


Figure S9. Concentration dependent ^{1}H-NMR data of DADA quadruple H-bonding array **2**: (a) H_a; (b) H_b; (c) H_c; (d) H_d.

Table S2. K_{dim} value of DADA quadruple H-bonding array **2**.

Signal	K_{dim} (M^{-1})	δ_m (ppm)	δ_d (ppm)	Adjusted r^2
H_a	300 ± 50	9.80 ± 0.02	10.31 ± 0.01	0.9907
H_b	300 ± 50	9.00 ± 0.02	9.80 ± 0.02	0.9919
H_c	200 ± 60	9.15 ± 0.02	9.59 ± 0.02	0.9786
H_d	200 ± 50	8.146 ± 0.001	8.202 ± 0.002	0.9882
	300 ± 100 (average)			

3.4. K_{ass} of supramolecular polymer **3** in 2% $CD_3OH/CDCl_3$

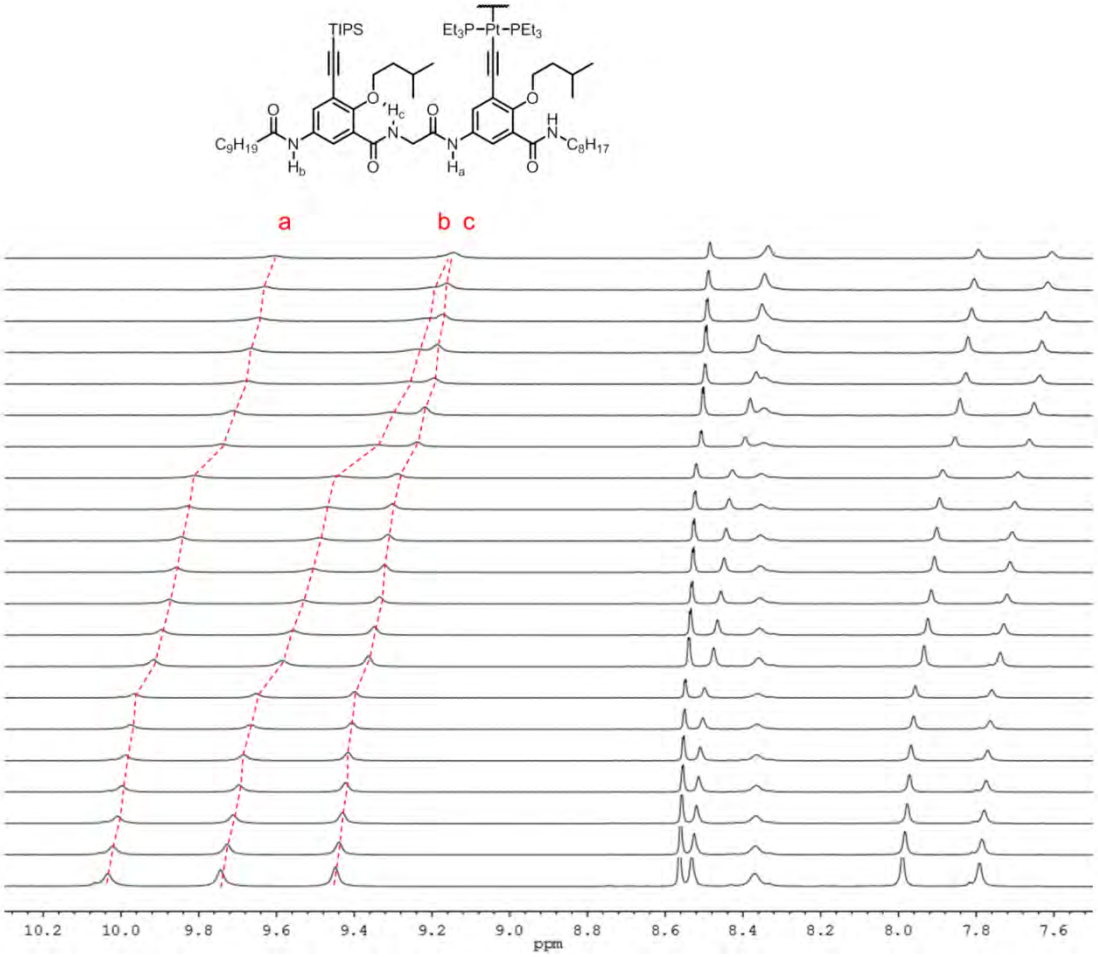


Figure S10. Stacked partial ^{1}H NMR spectra (700 MHz, 2% $CD_3OH/CDCl_3$) of supramolecular polymer **3** from 0.3 to 20 mM (from top to bottom).

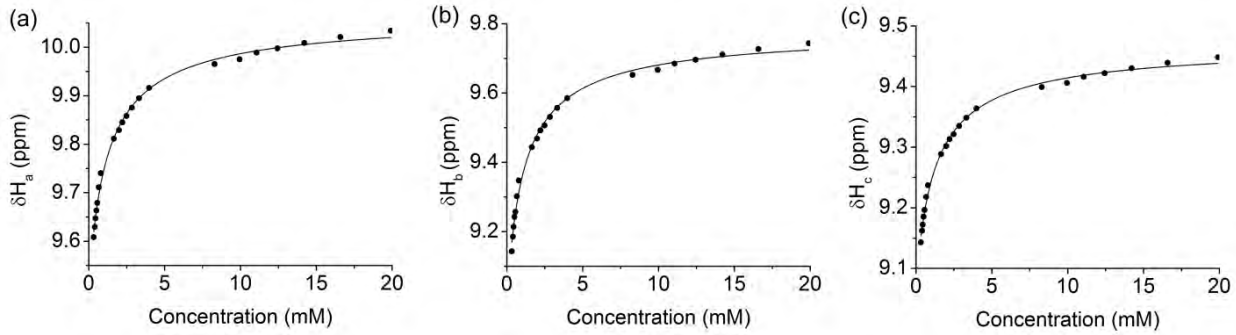


Figure S11. Concentration dependent ^{1}H-NMR data of supramolecular polymer **3**: (a) H_a; (b) H_b; (c) H_c.

Table S3. K_{ass} value of supramolecular polymer **3** based on the isodesmic model

Signal	K_{ass} (M^{-1})	δ_m (ppm)	δ_d (ppm)	Adjusted r^2
H_a	470 ± 50	9.49 ± 0.02	10.064 ± 0.007	0.9959
H_b	530 ± 60	8.97 ± 0.03	9.78 ± 0.01	0.9948
H_c	460 ± 40	9.06 ± 0.01	9.470 ± 0.005	0.9959
	490 ± 90 (average)			

3.5. K_{ass} of supramolecular ladder polymer **1** in 2% $CD_3OH/CDCl_3$

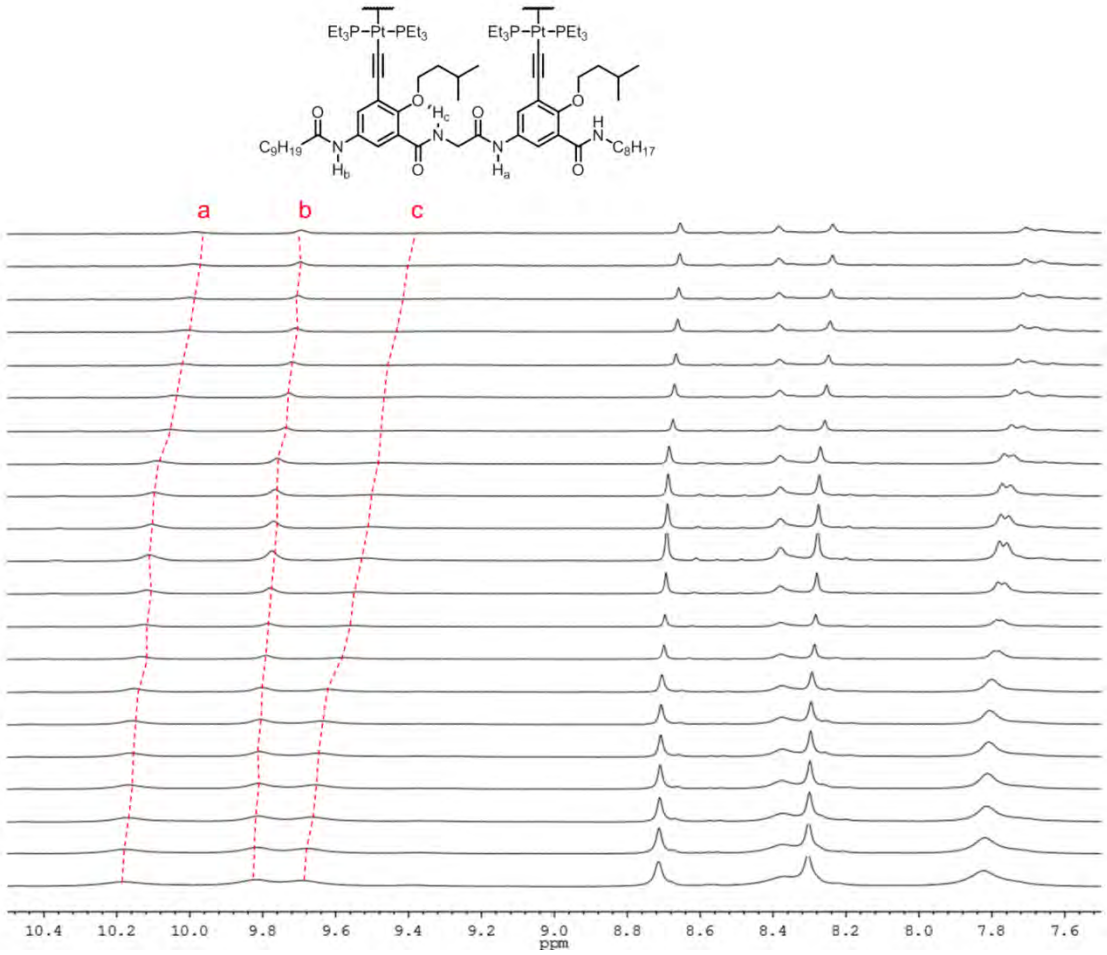


Figure S12. Stacked partial ^{1}H NMR spectra (700 MHz, 2% $CD_3OH/CDCl_3$) of supramolecular ladder polymer **1** from 0.3 to 18 mM (from top to bottom).

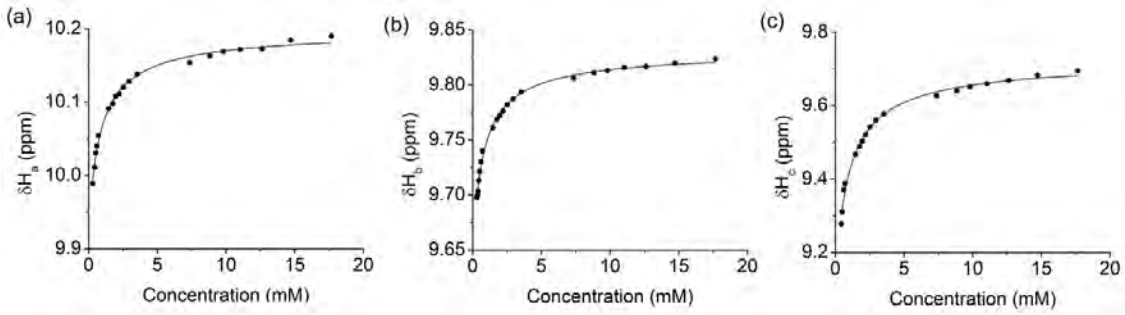


Figure S13. Concentration dependent ^{1}H-NMR data of supramolecular ladder polymer **1**: (a) H_a; (b) H_b; (c) H_c.

Table S4. K_{ass} value of supramolecular polymer **1** based on the isodesmic model

Signal	K_{ass} (M^{-1})	δ_m (ppm)	δ_{agg} (ppm)	Adjusted r^2
H_a	700 ± 100	9.92 ± 0.01	10.198 ± 0.004	0.9924
H_b	770 ± 90	9.641 ± 0.007	9.831 ± 0.002	0.9894
H_c	600 ± 100	9.09 ± 0.04	9.72 ± 0.01	0.9897
	700 ± 200 (average)			

3.6. Estimation of DP for supramolecular ladder polymer **1**

Based on the isodesmic model, the weight-average degree of polymerization DP_w can be estimated by the association constant K_{ass} and the initial concentration c_t.

$$DP_w = \sqrt{1 + 4K_{ass}c_t}$$

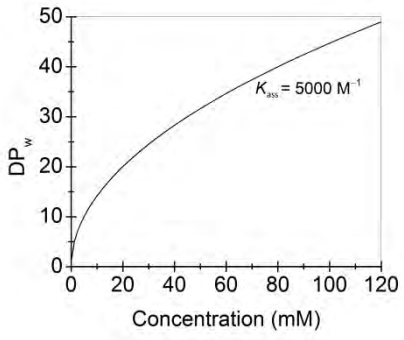


Figure S14. Plot of theoretical DP_w against initial concentration at K_{ass} = 5000 M^{-1}.

4. Size exclusion chromatography

SEC analyses were conducted on Styragel columns (HR1, HR2, HR3, and HR4 7.8 × 300 mm in serial) at 40 °C using THF as eluent with flow rate 1.0 mL/min on a HPLC pump equipped with a UV absorbance detector. The concentrations of the injected samples were 1 mg/mL. Under such a highly diluted concentration, compounds **1** and **4** are expected to exist in the monomeric state.

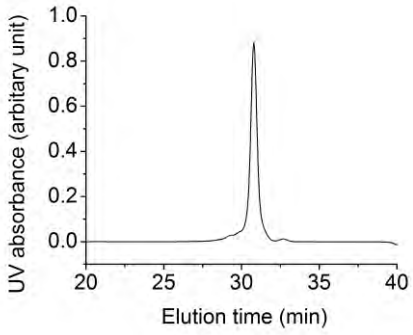


Figure S15. Size exclusion chromatogram of compound **4**.

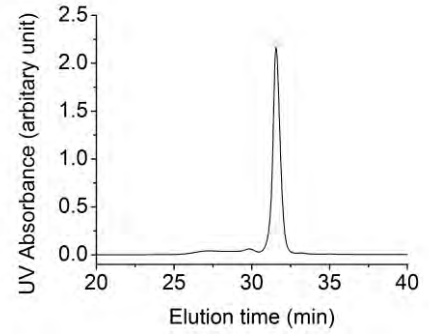


Figure S16. Size exclusion chromatogram of metallomacrocycle **1**.

5. Differential scanning calorimetry

The analysis was carried out on a differential scanning calorimeter and the sample was purged with N_2 during the analysis. The scan rate is 10 °C/min.

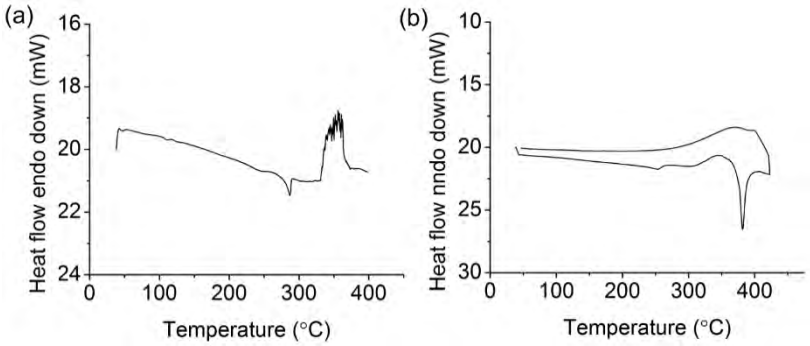


Figure S17. DSC curves of (a) supramolecular polymer **3** and (b) supramolecular ladder polymer **1**.

6. Viscosity measurements

Viscometry measurements were performed on an Ubbelohde viscometer in either pure $CHCl_3$ or 2% $CH_3OH/CHCl_3$ at 25.0 °C as specified in the paper.

7. Dynamic light scattering experiments

Dynamic light scattering (DLS) experiments were performed on a modified commercial LLS spectrometer equipped with a multi-τ digital time correlator and a cylindrical 22 mW UNIPHASE He-Ne laser (λ_0 = 632 nm). The solution of the supramolecular ladder polymer **1** in 5% $CH_3OH/CHCl_3$ was filtered through a 220 nm PTFE membrane before measurements.

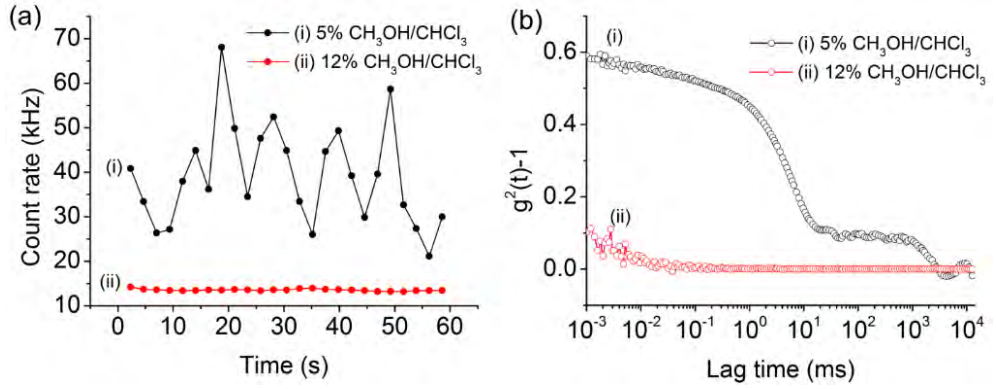


Figure S18. (a) Count rate fluctuation and (b) autocorrelation function of supramolecular ladder polymer **1** in (i) 5% $CH_3OH/CHCl_3$ and (ii) 12% $CH_3OH/CHCl_3$.

8. Scanning electron microscopy

Scanning electron microscopic analysis of the sample solution was prepared by drop-casting on a silicon wafer, air-dried and then coated with Au particle using an Ion Sputter Coater. The images were obtained by an electron microscope. Energy-dispersive X-ray spectroscopy was employed to determine the elemental composition of the micron sized spheres obtained from the supramolecular ladder polymer **1**.

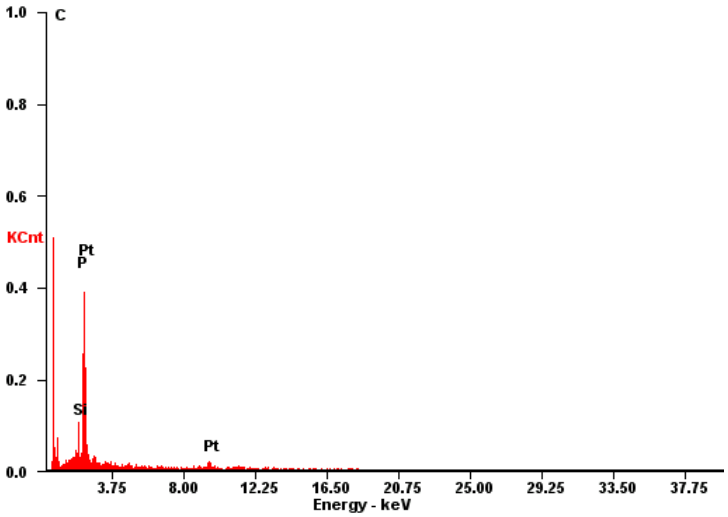


Figure S19. EDX spectrum of supramolecular ladder polymer **1**.

Table S5. Elemental analysis result of supramolecular ladder polymer **1** by EDX.[a]

Element	Theoretical value	Measured value
C	58.66	67.52
O	7.81	7.08
P	5.04	4.35
Pt	15.88	20.03

[a] The observed electron transition for the elements were K_{α}.

9. UV spectroscopy

UV spectra of supramolecular polymer **3** were measured on a 100 UV-Vis spectrometer in spectrophotometric grade $CHCl_3$ at 25 °C.

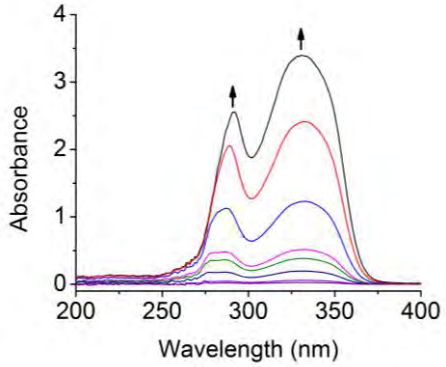


Figure S20. Stacked UV spectra of supramolecular polymer **3** in $CHCl_3$ at different concentrations (0.6 – 90 μM).

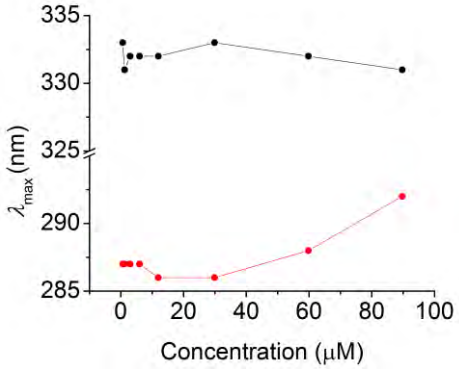


Figure S21. Plot of absorption maxima λ_{max} of supramolecular polymer **3** against concentration. The two absorption bands at ~ 292 and ~ 331 nm were assigned to π→π* transitions of the aromatic rings and metal-to-ligand charge transfer (MLCT) of the platinum(II) acetylide, respectively

10. X-ray crystal structure of compound **2** ($R_1 = R_2 = Me$)

Single crystal of **2** ($R_1 = R_2 = Me$) was obtained by slow evaporation from methanol/$CHCl_3$ and data were collected on a diffractometer using Mo Kα radiation.

X-ray crystal data for **2** ($R_1 = R_2 = Me$)•$CHCl_3$: $C_{43}H_{61}Cl_3N_4O_6Si$; M = 864.40; triclinic; a = 9.7693(4), b = 11.7068(5), c = 21.0929(9) Å; α = 98.8445(19), β = 90.879(2), γ = 93.088(2)°; V = 2395.78(17) $Å^3$; space group P-1; Z = 2; ρ_{calcd} = 1.197 Mg m^{-3}; T = 296(2) K; λ ($Mo_{K\alpha}$) = 1.54178 Å; 70105 reflections collected; 8786 independent reflections; R_{int} = 0.0651; observed data with I ≥ 2σ(I) = 8786; R_1 = 0.0826, wR_2 = 0.2421 [I ≥ 2σ(I)]. CCDC-1026059 contains the supplementary crystallographic data for **2** ($R_1 = R_2 = Me$)•$CHCl_3$.

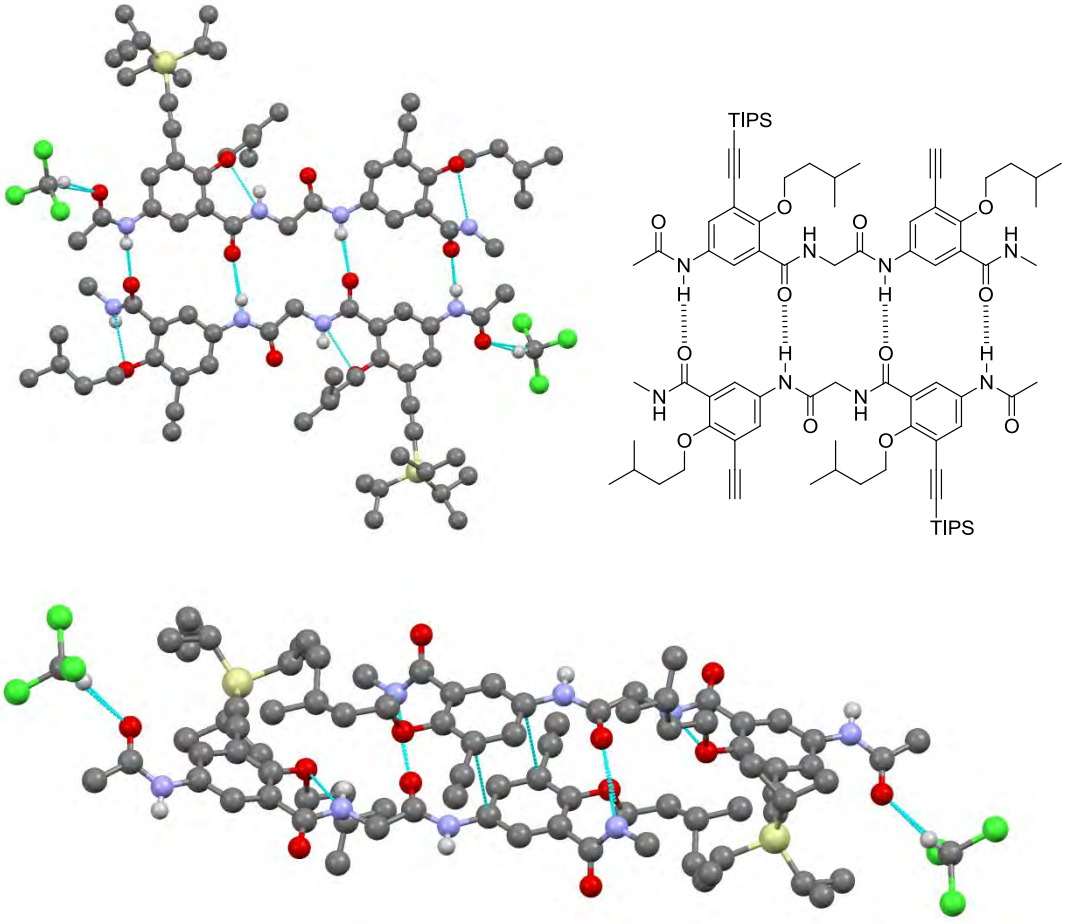
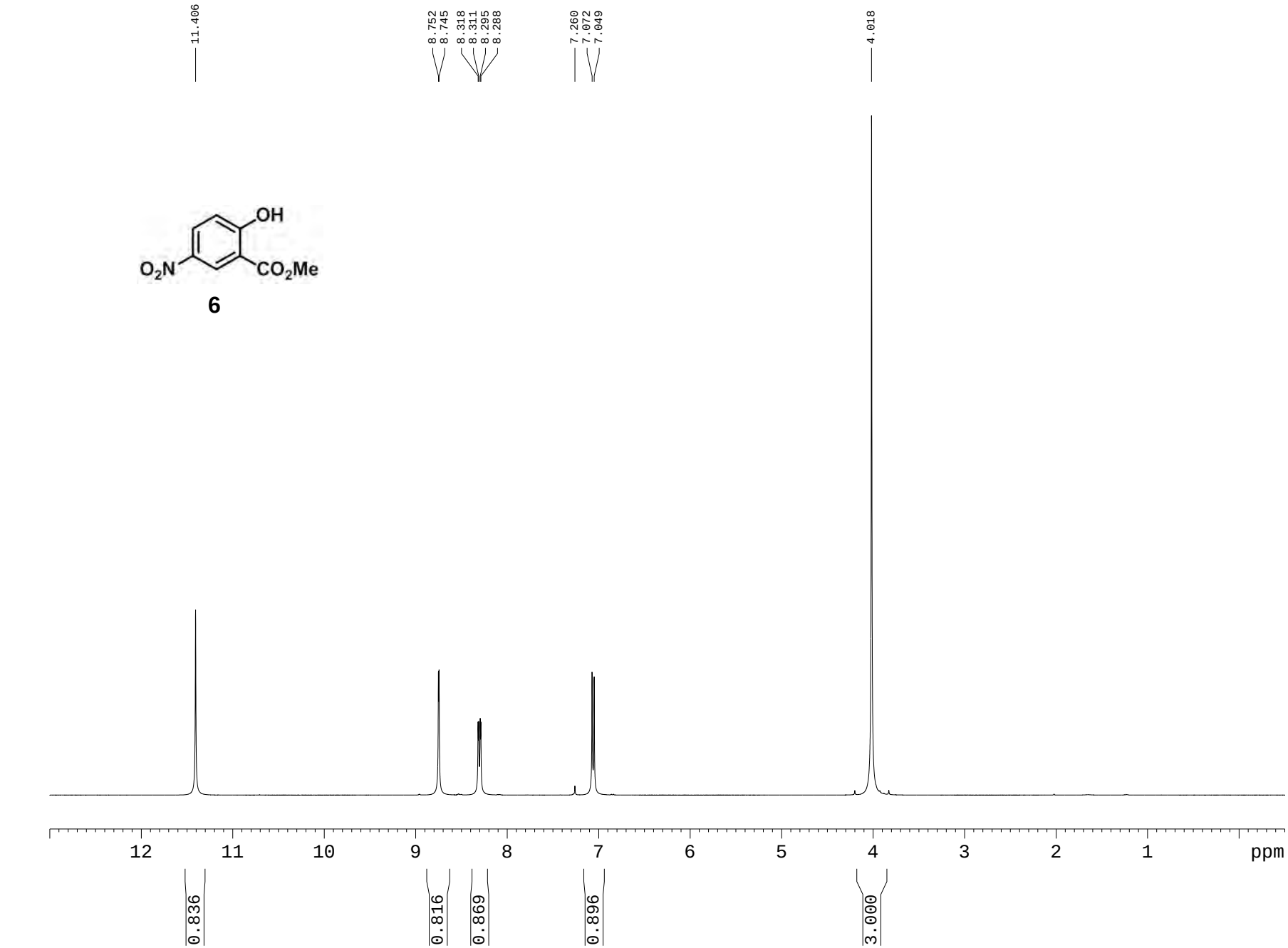


Figure S22. X-ray crystal structure of compound **2** ($R_1 = R_2 = Me$) (top) showing the quadruple H-bonding interaction between two molecules of **2** on the same plane, and (bottom) π–π stacking interaction between two molecules of **2** on different plane.

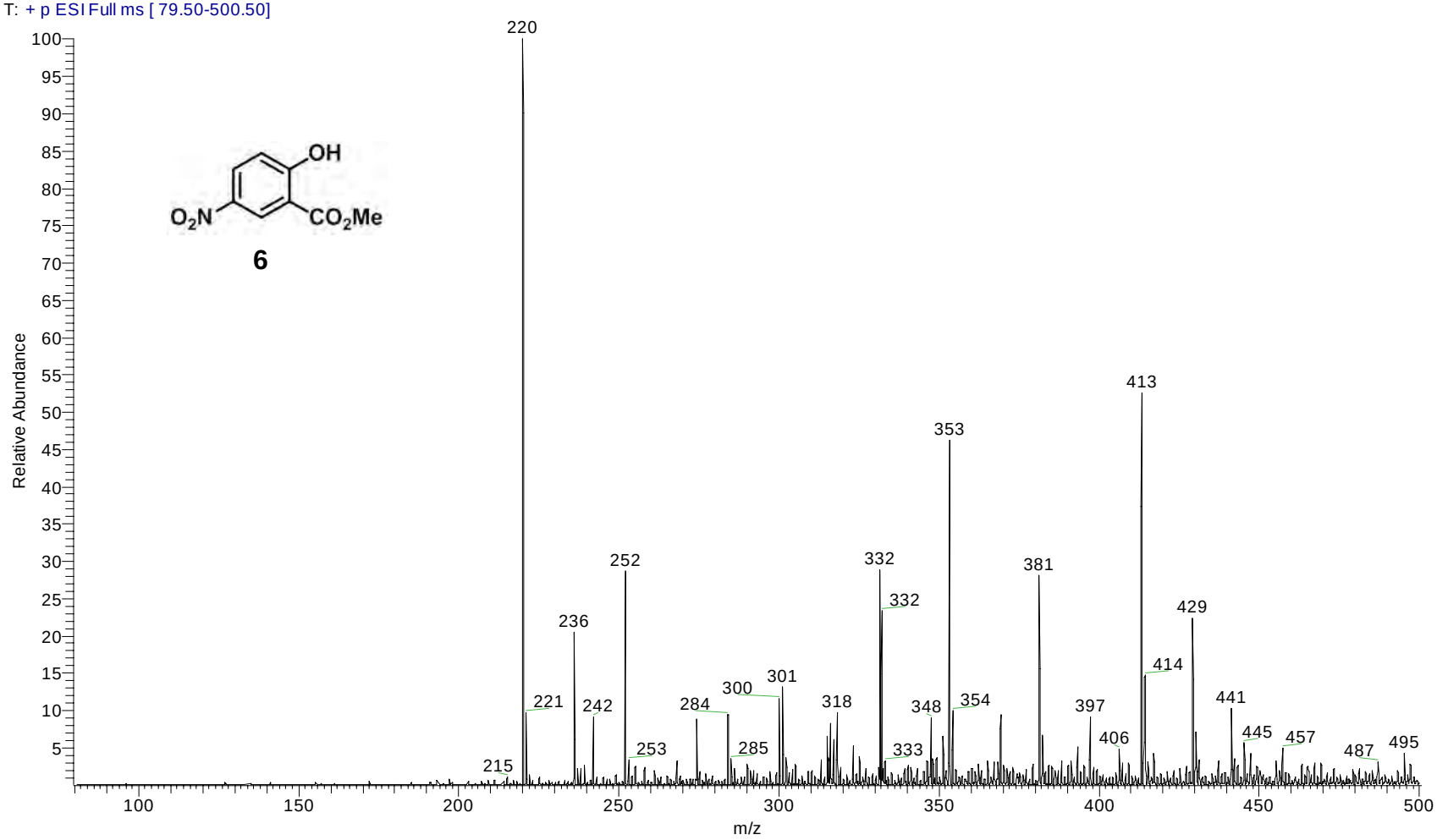
11. List of NMR and MS spectra

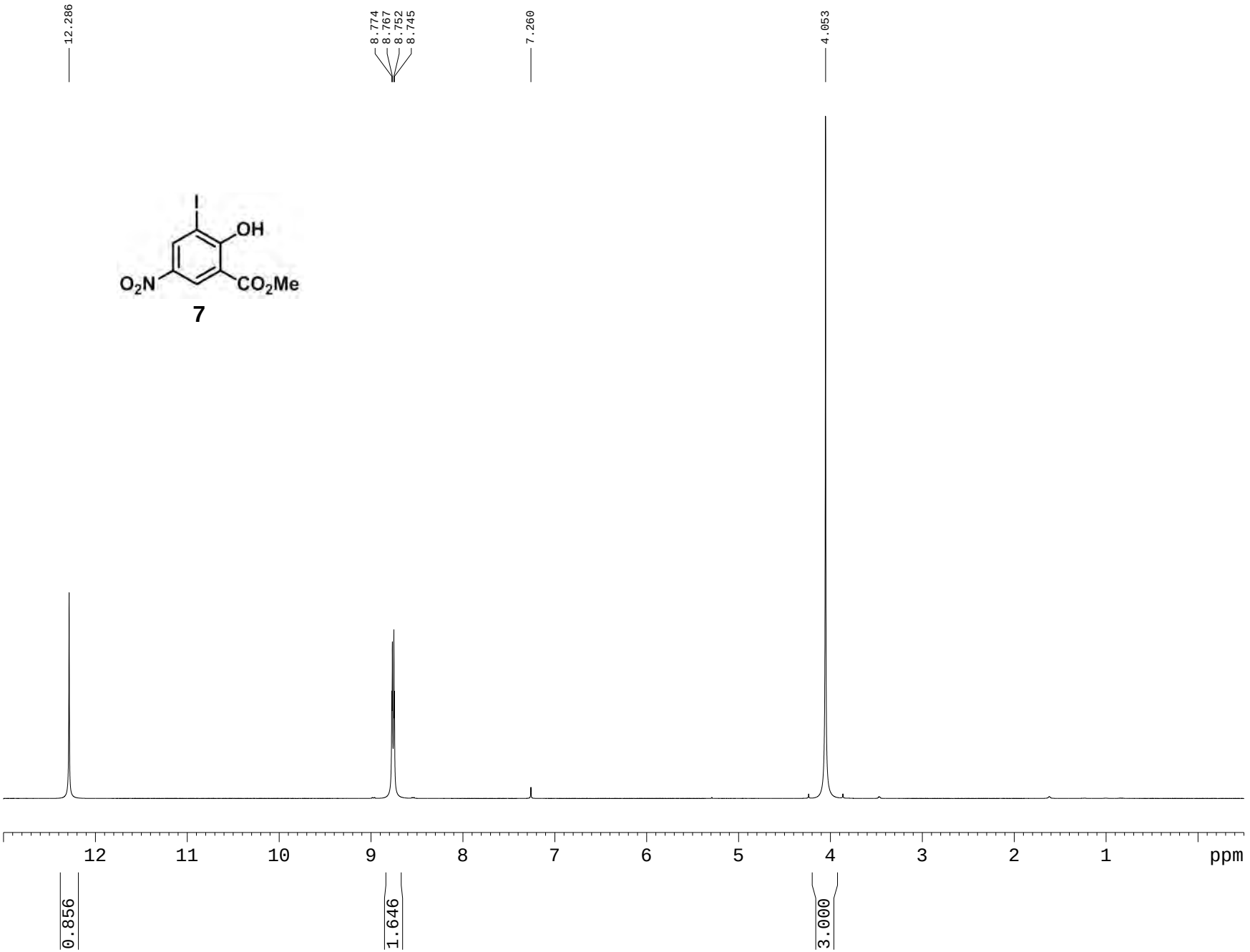

11.406
8.752
8.745
8.318
8.311
8.295
8.288
7.260
7.072
7.049
4.018
OH
O_2N
CO_2Me
6
BRUKER
NAME Sun-17122011-(OH)-NO2-CO2Me
EXPNO 1
PROCNO 1
Date_ 20111217
Time 10.54
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 57
DW 60.800 usec
DE 6.50 usec
TE 294.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 7.10 usec
PL1 -2.00 dB
PL1W 13.17734718 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300099 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
12
11
10
9
8
7
6
5
4
3
2
1
ppm
0.836
0.816
0.869
0.896
3.000

169.379
166.283
140.072
130.612
126.710
118.706
112.188
77.478
77.160
76.842
53.232
OH
O_2N
CO_2Me
6
BRUKER
NAME Sun-17122011-(OH)-NO2-CO2Me
EXPNO 2
PROCNO 1
Date_ 20111217
Time 10.56
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 2686
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 294.8 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 14.50 usec
PL1 -4.00 dB
PL1W 90.22689819 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 20.06 dB
PL13 22.00 dB
PL2W 13.17734718 W
PL12W 0.08200268 W
PL13W 0.05245997 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127604 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

D:\MS_raw_data\hfc2009_131016161047 10/16/13 04:10:47 PM OH, NO2-CO2Me
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

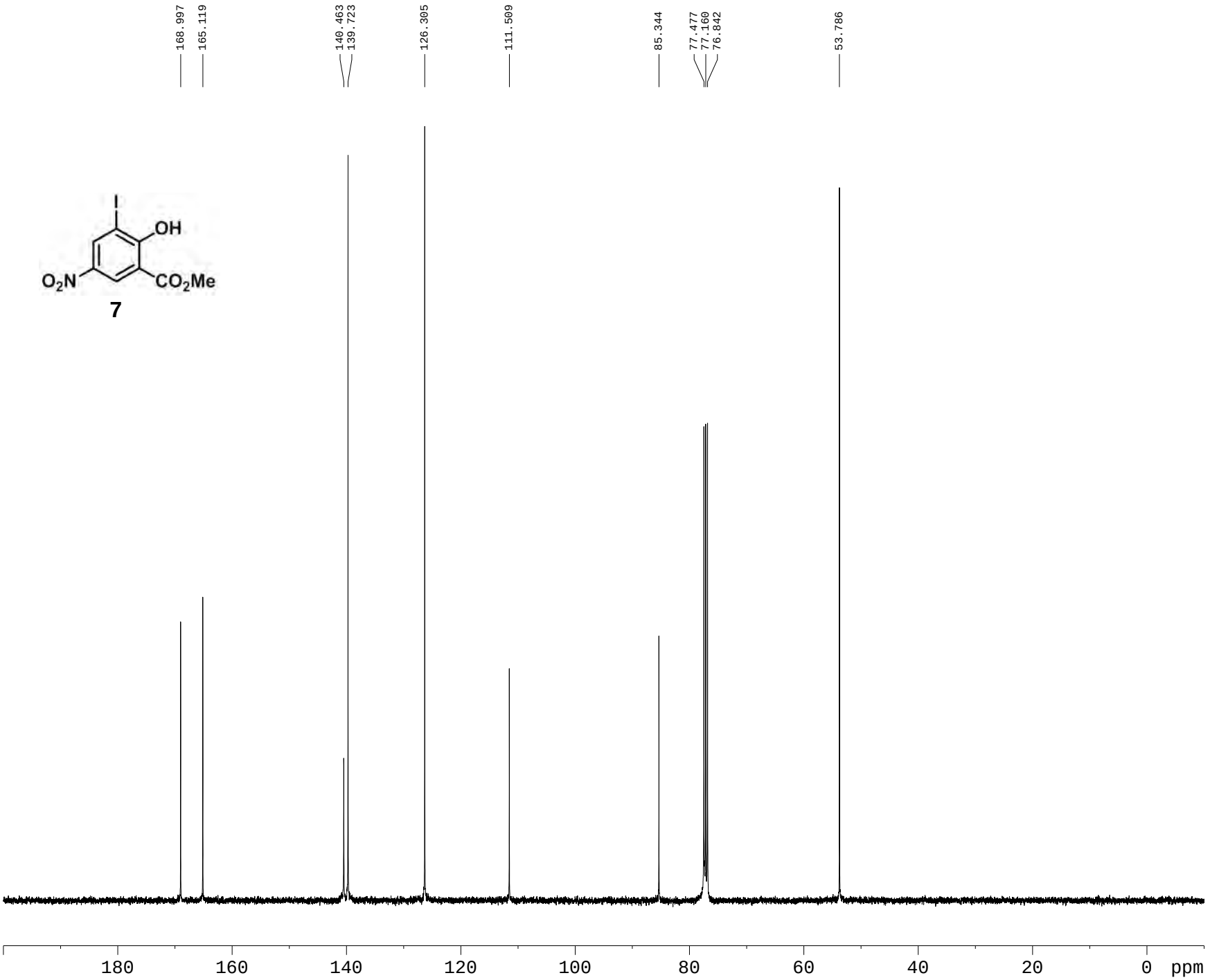
hfc2009_131016161047 #3-8 RT: 0.29-0.71 AV: 6 SM: 5G NL: 1.64E5
T: + p ESI Full ms [79.50-500.50]





BRUKER

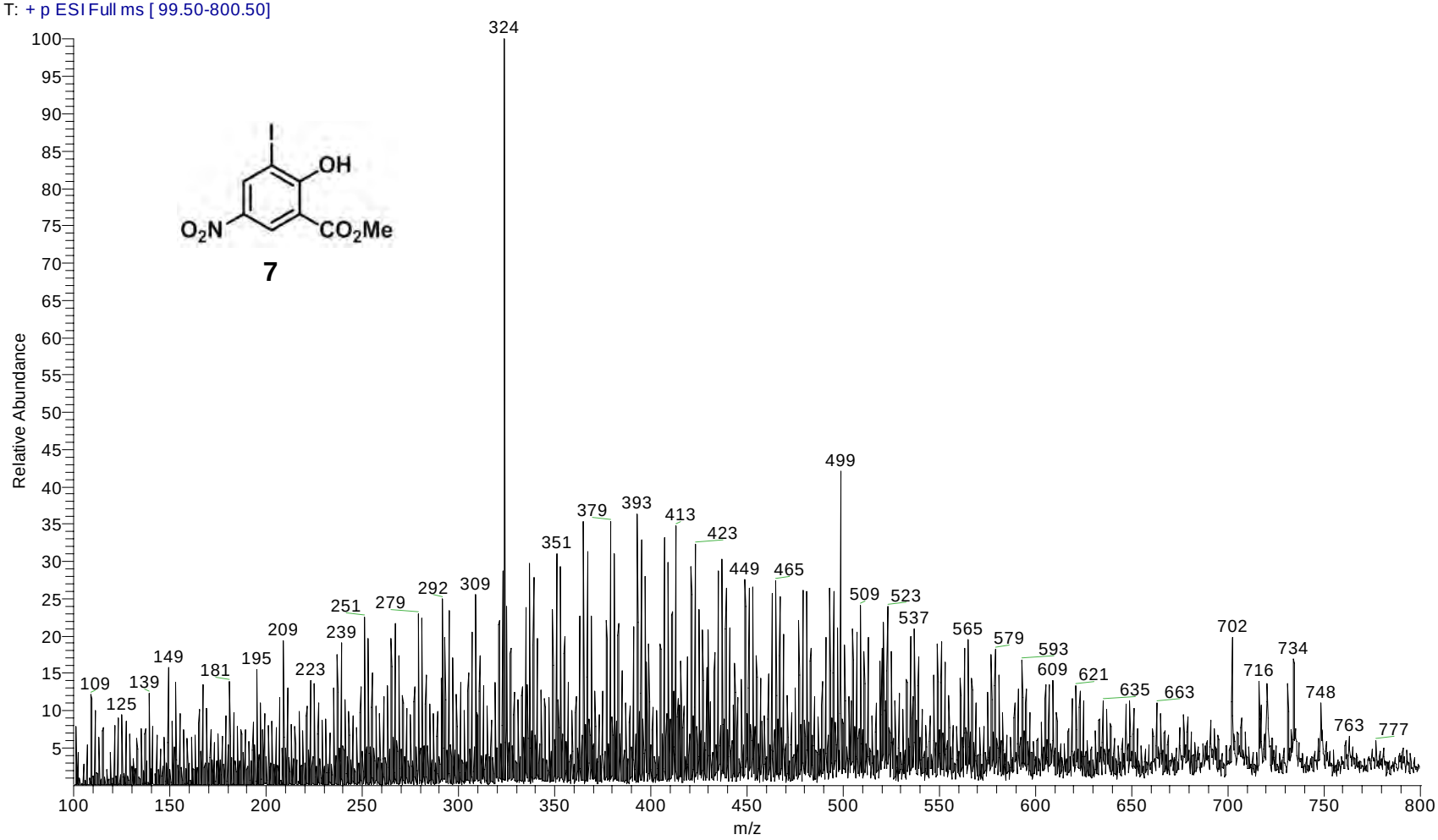
```
NAME        Sun-18122011-(I,OH)-NO2-CO2Me
EXPNO                   1
PROCNO                  1
Date_            20111218
Time                20.38
INSTRUM             spect
PROBHD   5 mm PABBI 1H/
PULPROG             zg30
TD                 32768
SOLVENT            CDCl3
NS                    32
DS                     2
SWH             8223.685 Hz
FIDRES          0.250967 Hz
AQ              1.9923444 sec
RG                  80.6
DW                60.800 usec
DE                 6.50 usec
TE                294.5 K
D1               1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 7.10 usec
PL1                -2.00 dB
PL1W          13.17734718 W
SFO1          400.1324710 MHz
SI                 32768
SF            400.1300099 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



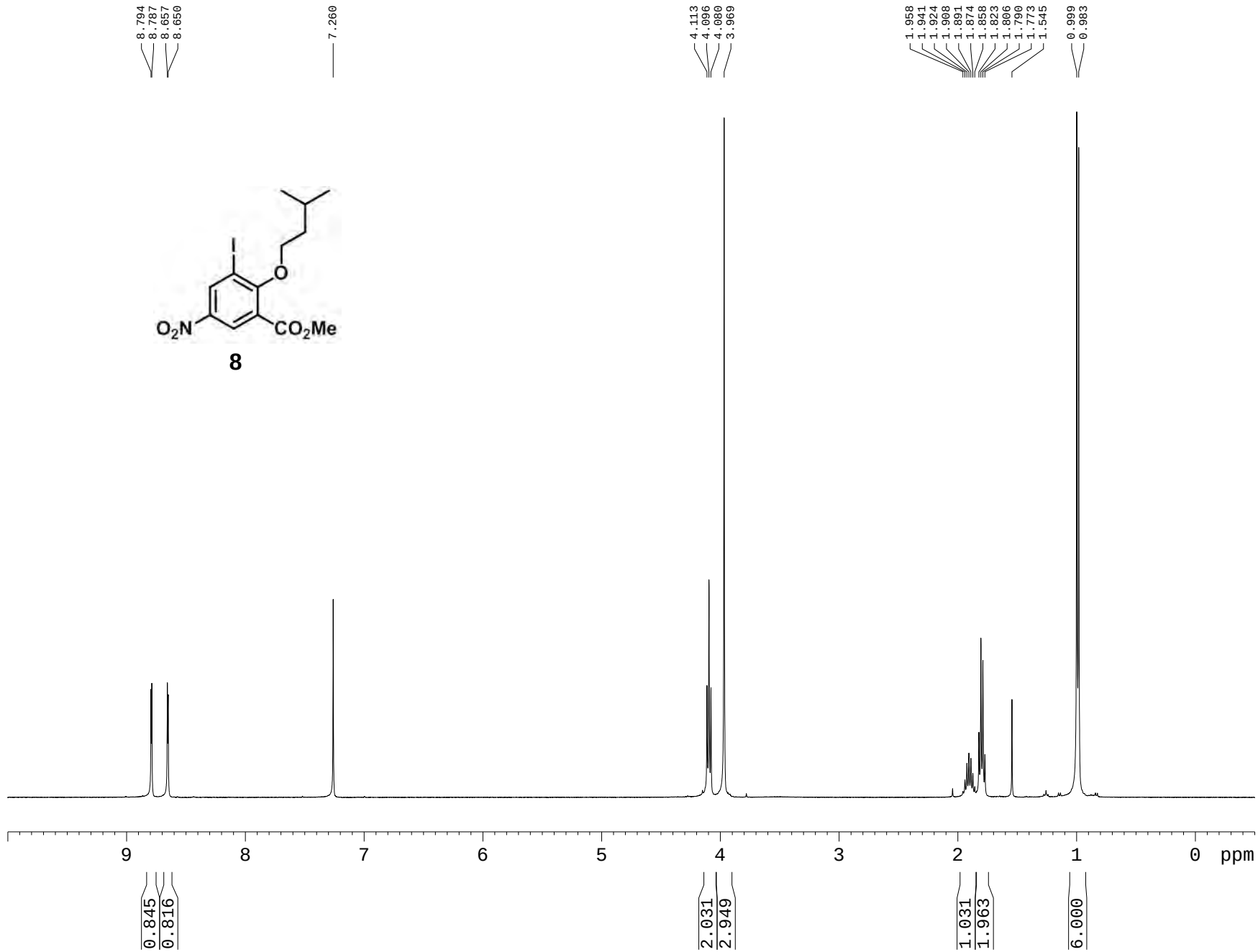

```
NAME        Sun-18122011-(I,OH)-NO2-CO2Me
EXPNO                    2
PROCNO                   1
Date_             20111218
Time                 20.43
INSTRUM              spect
PROBHD   5 mm PABBI 1H/
PULPROG              zgpg30
TD                    65536
SOLVENT               CDCl3
NS                     2120
DS                        4
SWH              24038.461 Hz
FIDRES            0.366798 Hz
AQ                1.3631988 sec
RG                      203
DW                   20.800 usec
DE                    6.50 usec
TE                   294.8 K
D1                2.00000000 sec
D11               0.03000000 sec
TD0                       1

======== CHANNEL f1 ========
NUC1                    13C
P1                    14.50 usec
PL1                   -4.00 dB
PL1W            90.22689819 W
SFO1           100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2              waltz16
NUC2                    1H
PCPD2                 90.00 usec
PL2                   -2.00 dB
PL12                  20.06 dB
PL13                  22.00 dB
PL2W            13.17734718 W
PL12W            0.08200268 W
PL13W            0.05245997 W
SFO2           400.1316005 MHz
SI                     32768
SF             100.6127624 MHz
WDW                       EM
SSB                        0
LB                     1.00 Hz
GB                         0
PC                     1.40
```

D:\MS_raw_data\hfc1481_120712113215 07/12/12 11:32:15 AM (I,OH)-NO2-CO2Me
esi pos, 3kV, 5ul/min, w/o sheath gas, unknown conc.

hfc1481_120712113215 #4 RT: 0.37 AV: 1 SM: 5G NL: 3.95E5
T: + p ESI Full ms [99.50-800.50]

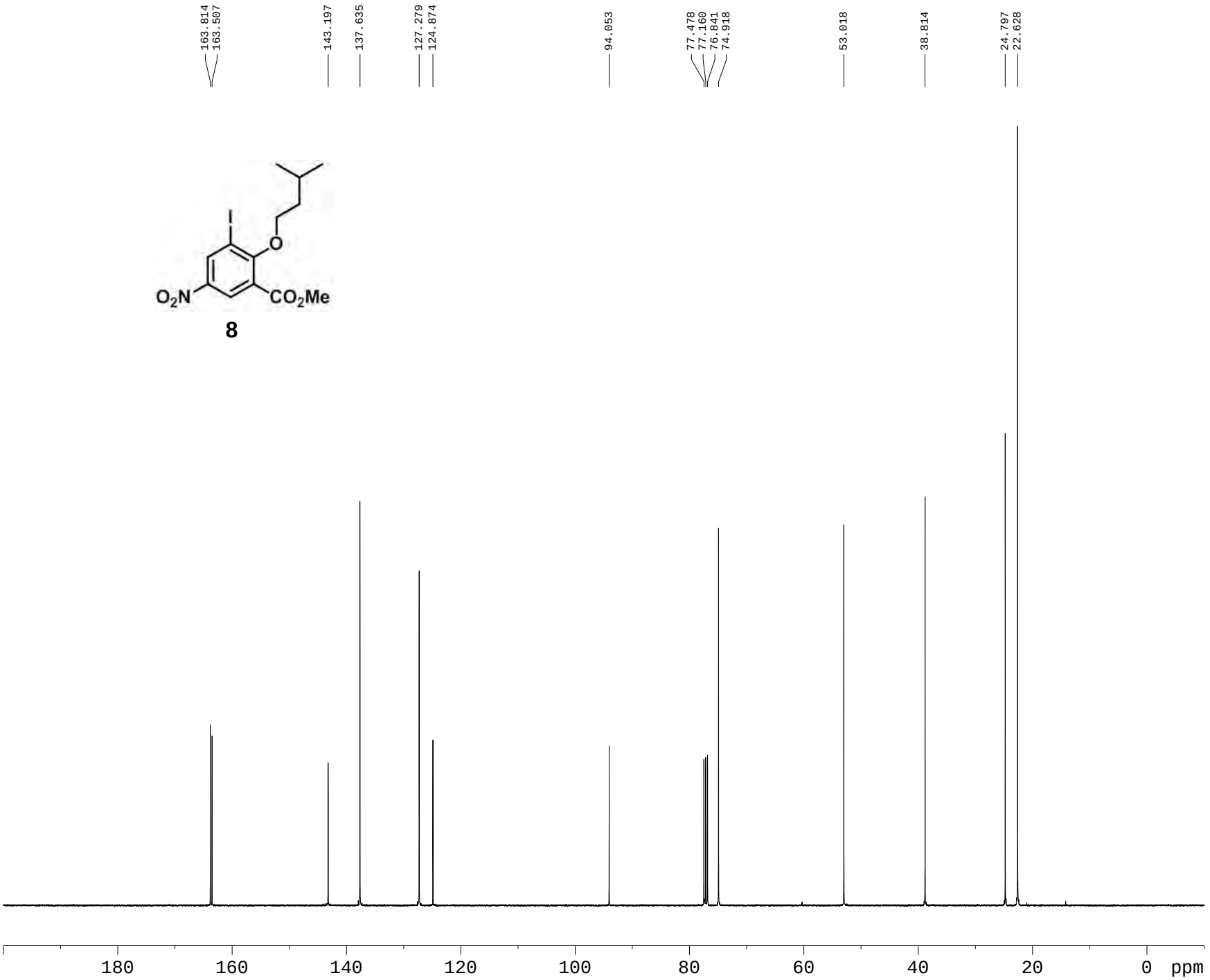


7



BRUKER

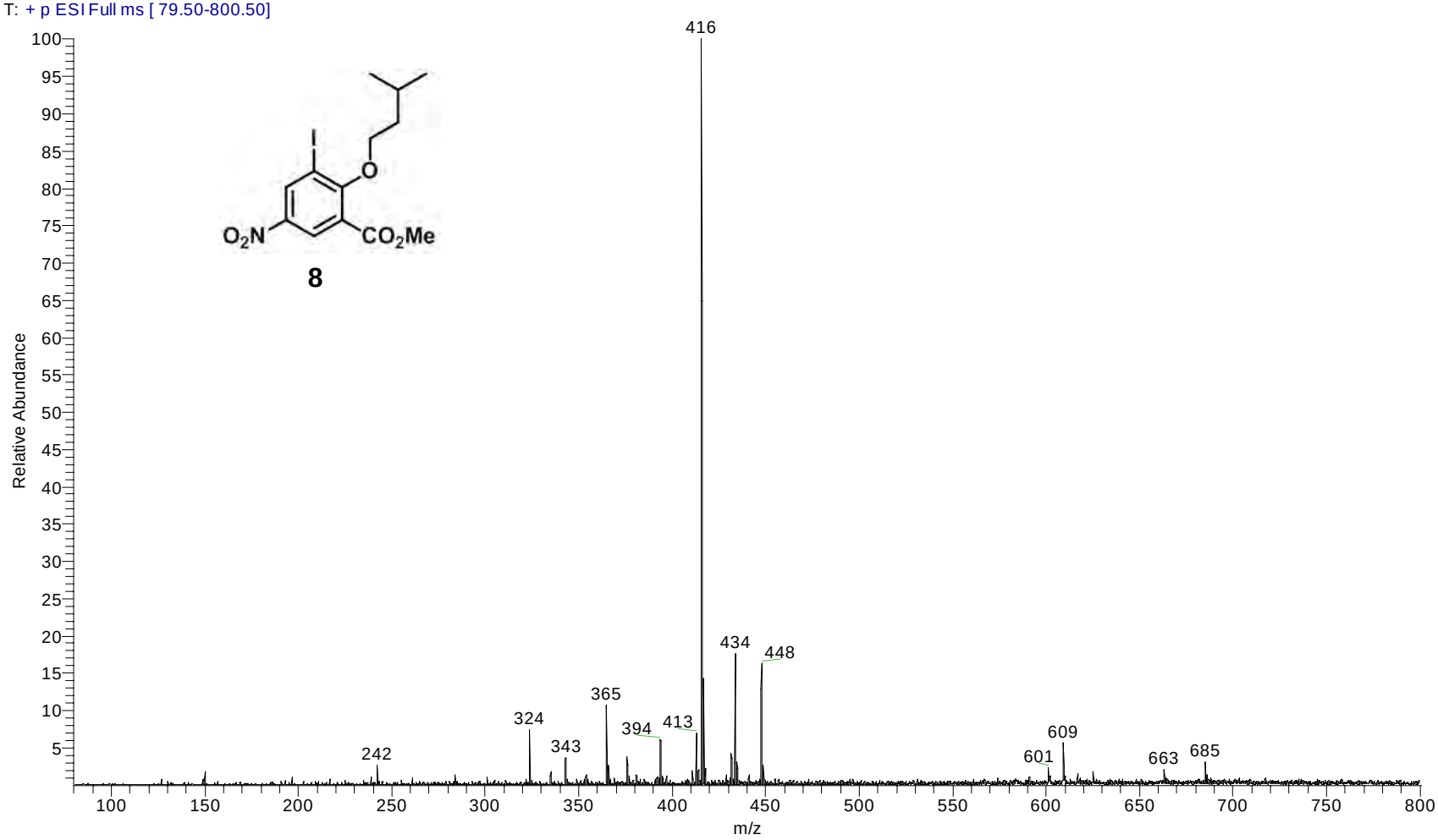
```
NAME        Sun-17012013-(I)-NO2-CO2Me
EXPNO                 1
PROCNO                1
Date_          20130117
Time              17.44
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                32768
SOLVENT           CDCl3
NS                   32
DS                    2
SWH            8223.685 Hz
FIDRES         0.250967 Hz
AQ             1.9923444 sec
RG                  144
DW                60.800 usec
DE                 6.50 usec
TE                296.0 K
D1             1.00000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                  1H
P1                14.00 usec
PL1               -1.00 dB
PL1W        13.56617069 W
SFO1        400.1924713 MHz
SI                32768
SF          400.1900146 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



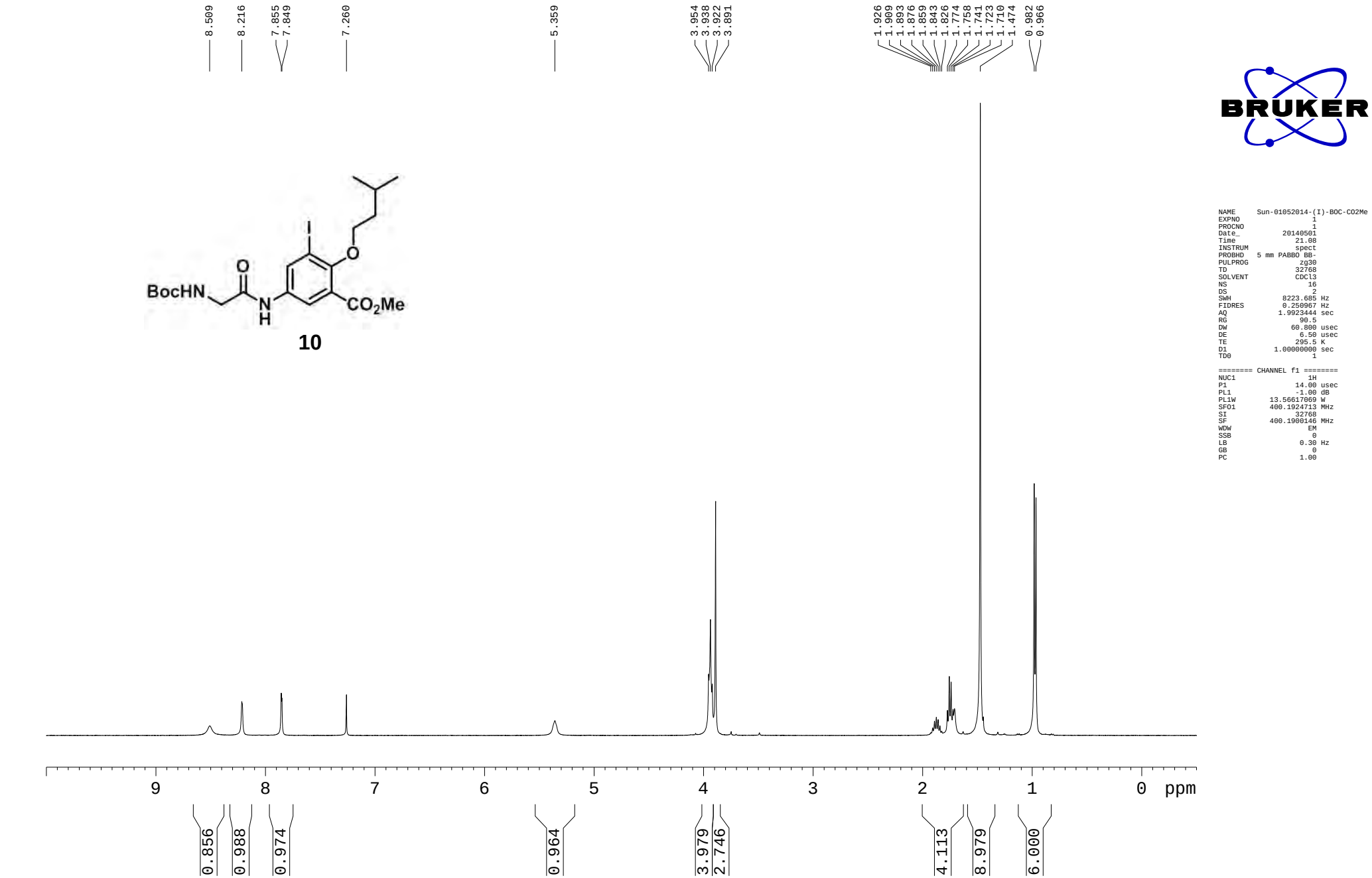

```
NAME          Sun-17012013-(I)-NO2-CO2Me
EXPNO                                  2
PROCNO                                 1
Date_                           20130117
Time                               22.55
INSTRUM                             spect
PROBHD     5 mm PABBO BB-
PULPROG                         zgpg30
TD                                 65536
SOLVENT                         CDCl3
NS                                   597
DS                                     4
SWH                          24038.461 Hz
FIDRES                        0.366798 Hz
AQ                            1.3631988 sec
RG                                   228
DW                               20.800 usec
DE                                6.50 usec
TE                               296.6 K
D1                            2.00000000 sec
D11                           0.03000000 sec
TD0                                    1

======== CHANNEL f1 ========
NUC1                               13C
P1                                9.90 usec
PL1                              -2.00 dB
PL1W                       55.33689499 W
SFO1                      100.6379183 MHz

======== CHANNEL f2 ========
CPDPRG2                       waltz16
NUC2                               1H
PCPD2                            90.00 usec
PL2                              -1.00 dB
PL12                             15.16 dB
PL13                             18.62 dB
PL2W                       13.56617069 W
PL12W                       0.32844096 W
PL13W                       0.14806664 W
SFO2                      400.1916008 MHz
SI                                32768
SF                        100.6278571 MHz
WDW                                EM
SSB                                   0
LB                                 1.00 Hz
GB                                    0
PC                                 1.40
```

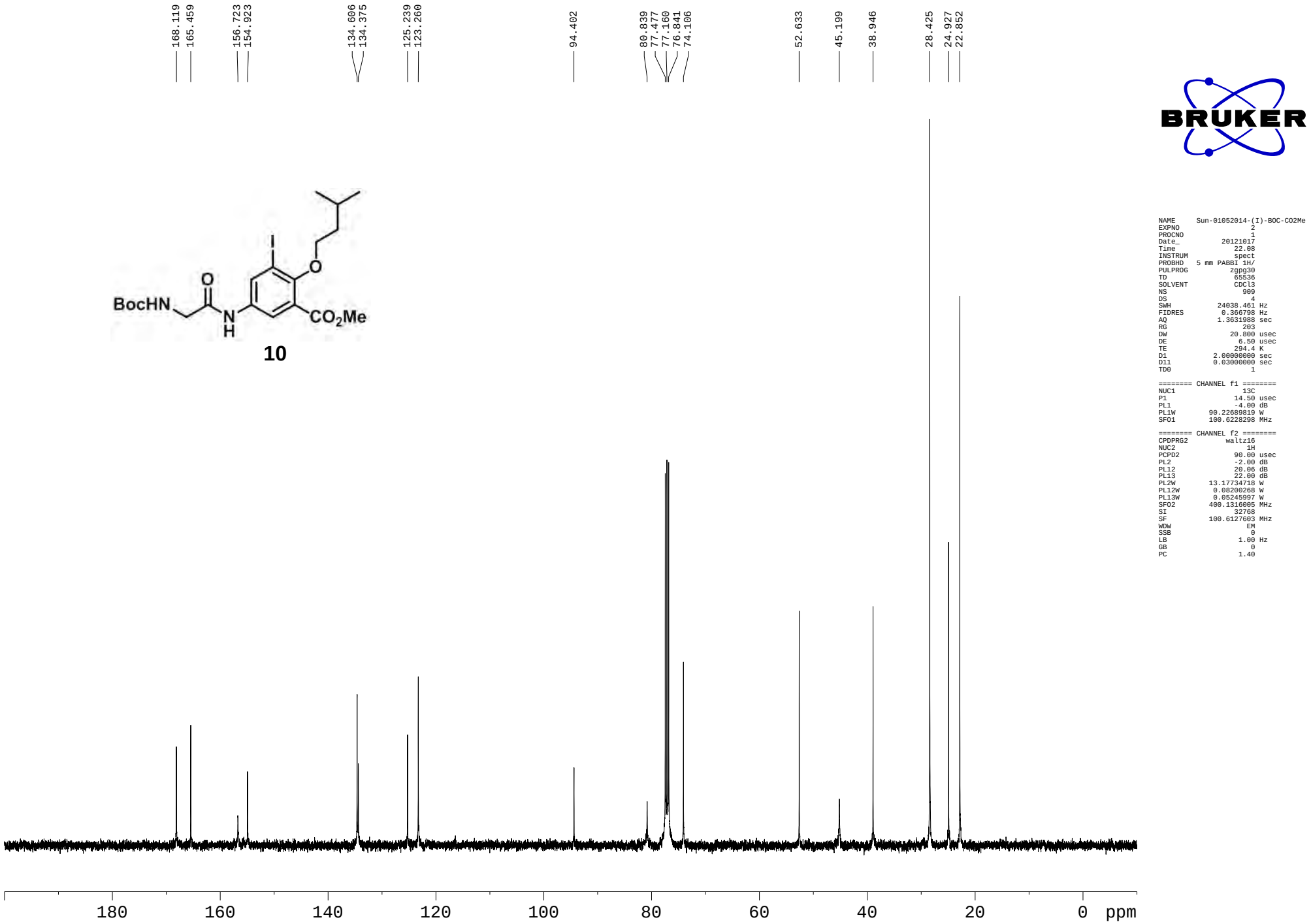
D:\MS_raw_data\hfc2049 01/04/14 04:26:08 PM (I,ic5)-NO2-CO2Me
ESI pos, 3kV, 3uL/min, w/o sheath gas, unknown conc

hfc2049 #5-7 RT: 0.46-0.63 AV: 3 SM: 5G NL: 1.13E6
T: + p ESI Full ms [79.50-800.50]



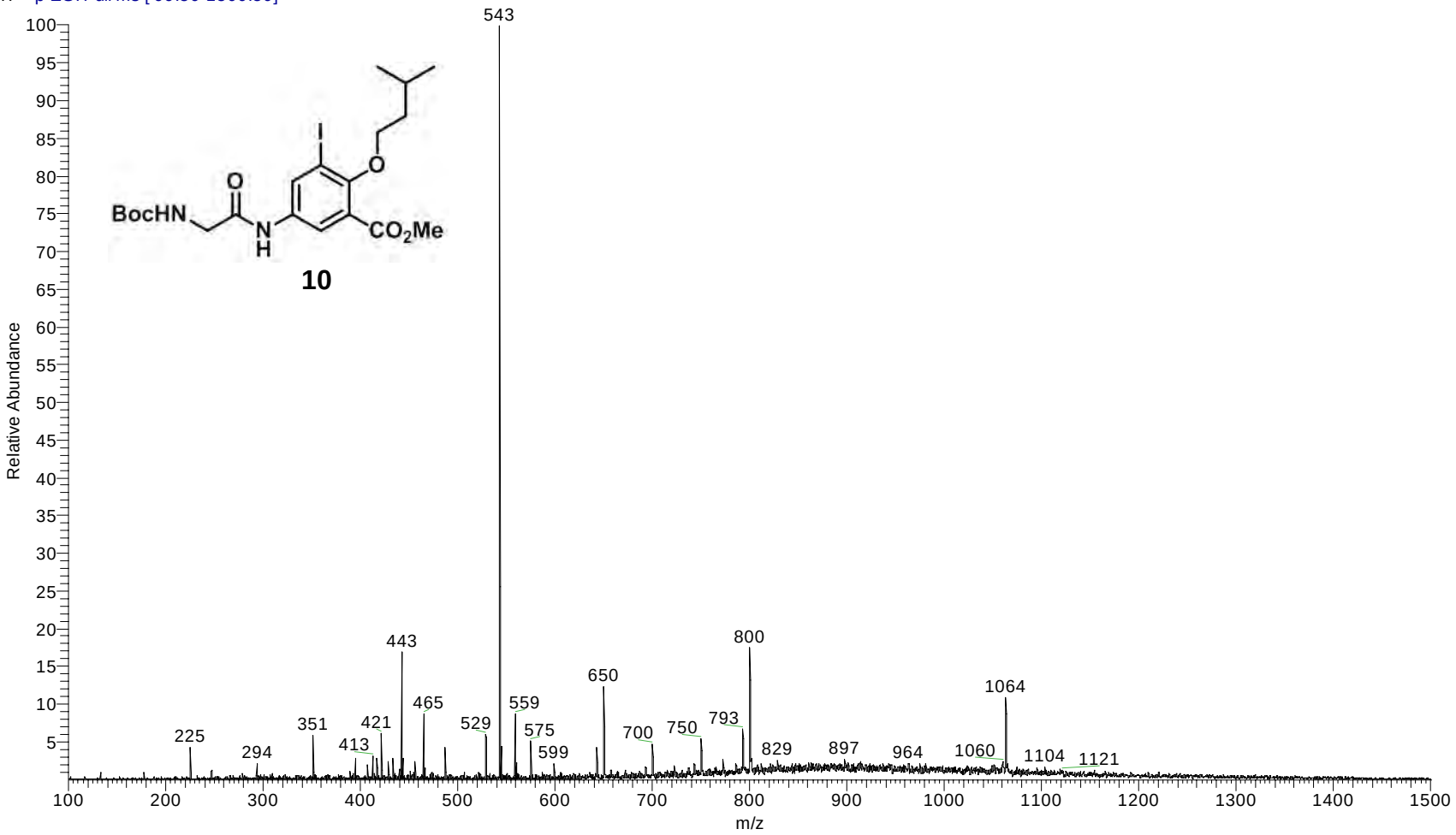
8

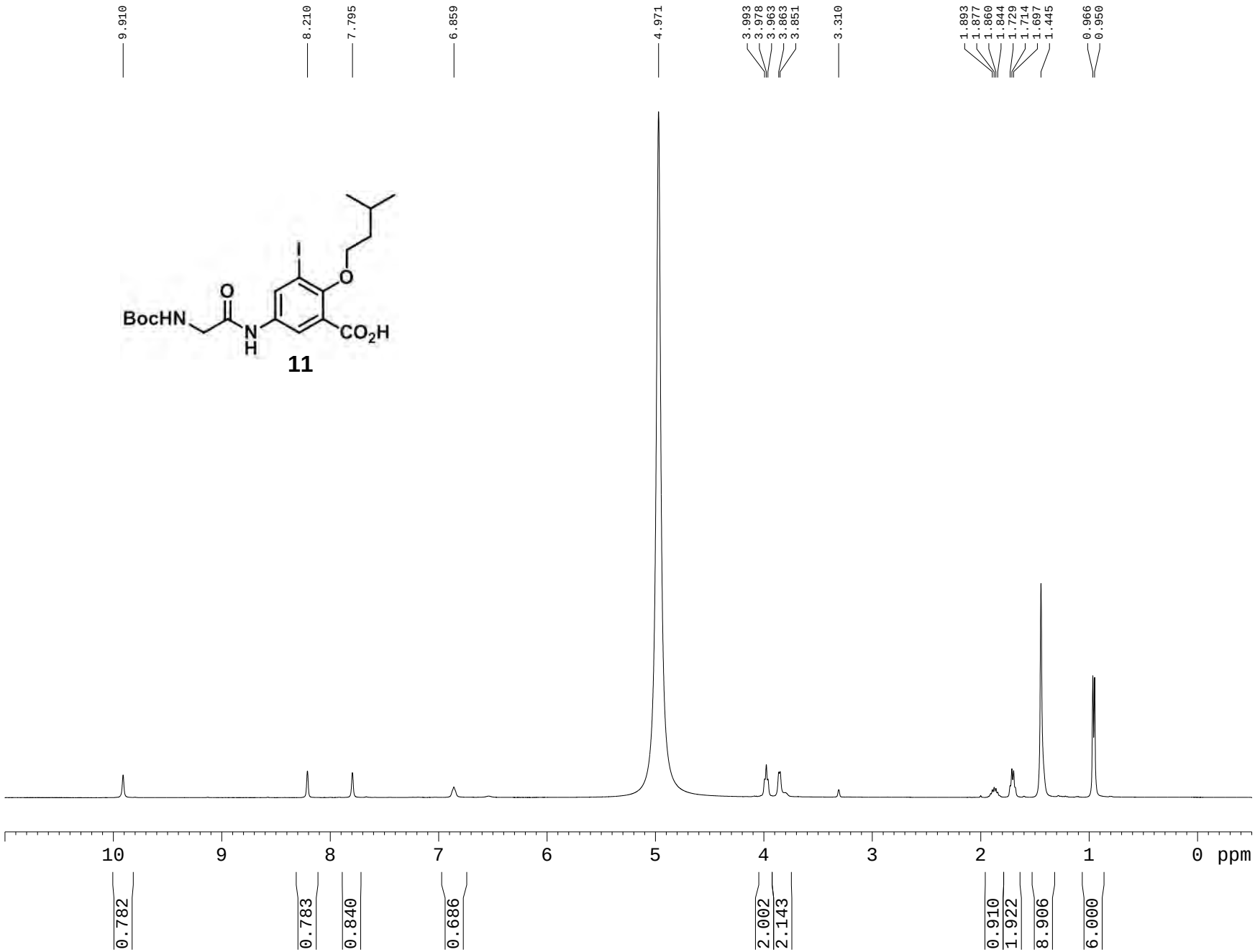

8.509
8.216
7.855
7.849
7.260
5.359
3.954
3.938
3.922
3.891
1.926
1.909
1.893
1.876
1.859
1.843
1.826
1.774
1.758
1.741
1.723
1.710
1.474
0.982
0.966
BocHN
O
N
H
I
O
CO2Me
10
NAME Sun-01052014-(I)-BOC-CO2Me
EXPNO 1
PROCNO 1
Date_ 20140501
Time 21.08
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 90.5
DW 60.800 usec
DE 6.50 usec
TE 295.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1900146 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
0.856
0.988
0.974
0.964
3.979
2.746
4.113
8.979
6.000


168.119
165.459
156.723
154.923
134.606
134.375
125.239
123.260
94.402
80.839
77.477
77.160
76.841
74.106
52.633
45.199
38.946
28.425
24.927
22.852
BocHN
O
N
H
O
I
CO2Me
10
NAME Sun-01052014-(I)-BOC-CO2Me
EXPNO 2
PROCNO 1
Date_ 20121017
Time 22.08
INSTRUM spect
PROBHD 5 mm PABBI 1H/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 909
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 294.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 14.50 usec
PL1 -4.00 dB
PL1W 90.22689819 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -2.00 dB
PL12 20.06 dB
PL13 22.00 dB
PL2W 13.17734718 W
PL12W 0.08200268 W
PL13W 0.05245997 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127603 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

D:\MS_raw_data\hfc1502 08/27/12 05:25:40 PM (I,ic5)-BOC-CO2Me
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

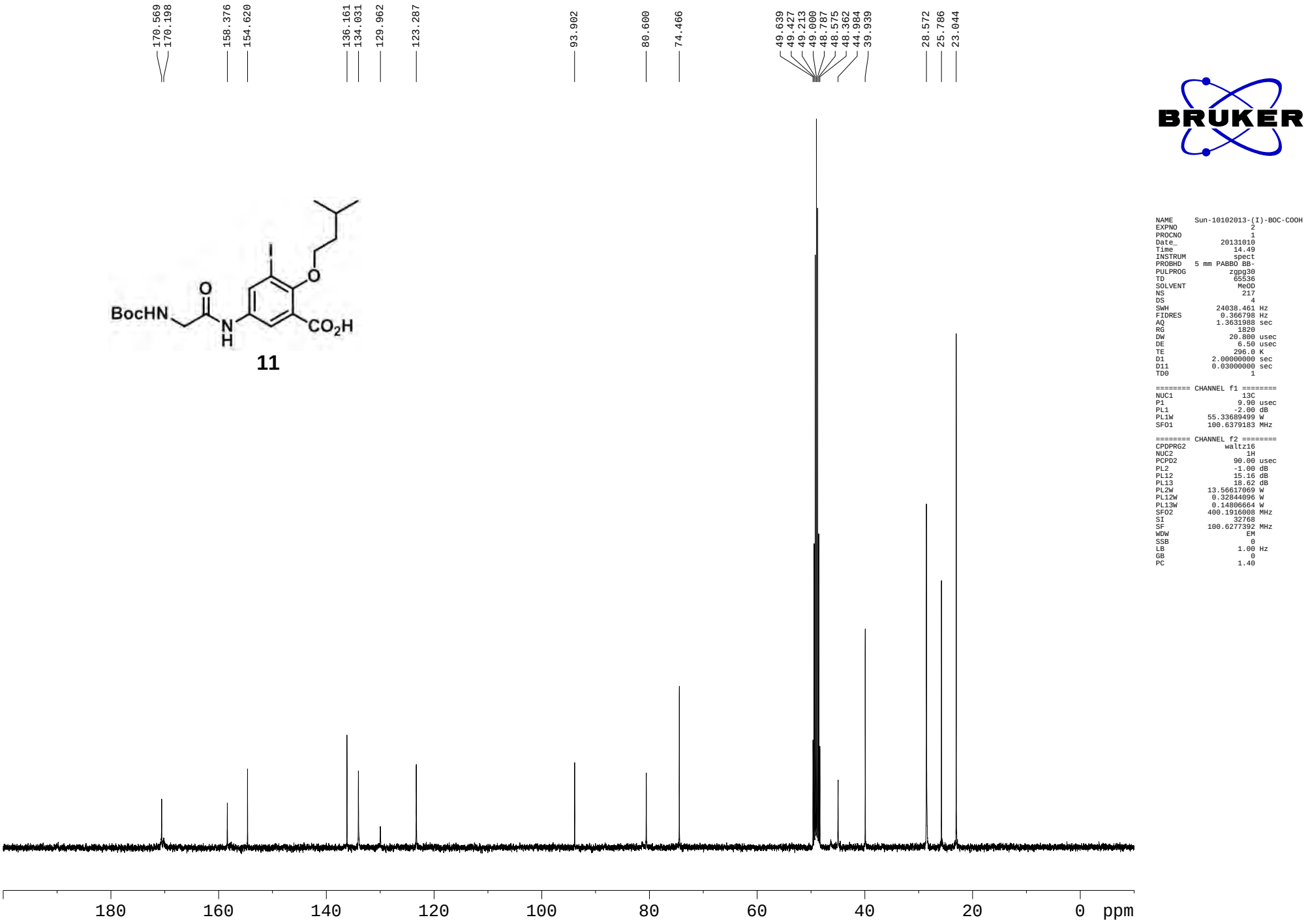
hfc1502 #6-8 RT: 0.53-0.69 AV: 3 SM: 5G NL: 1.84E6
T: + p ESI Full ms [99.50-1500.50]





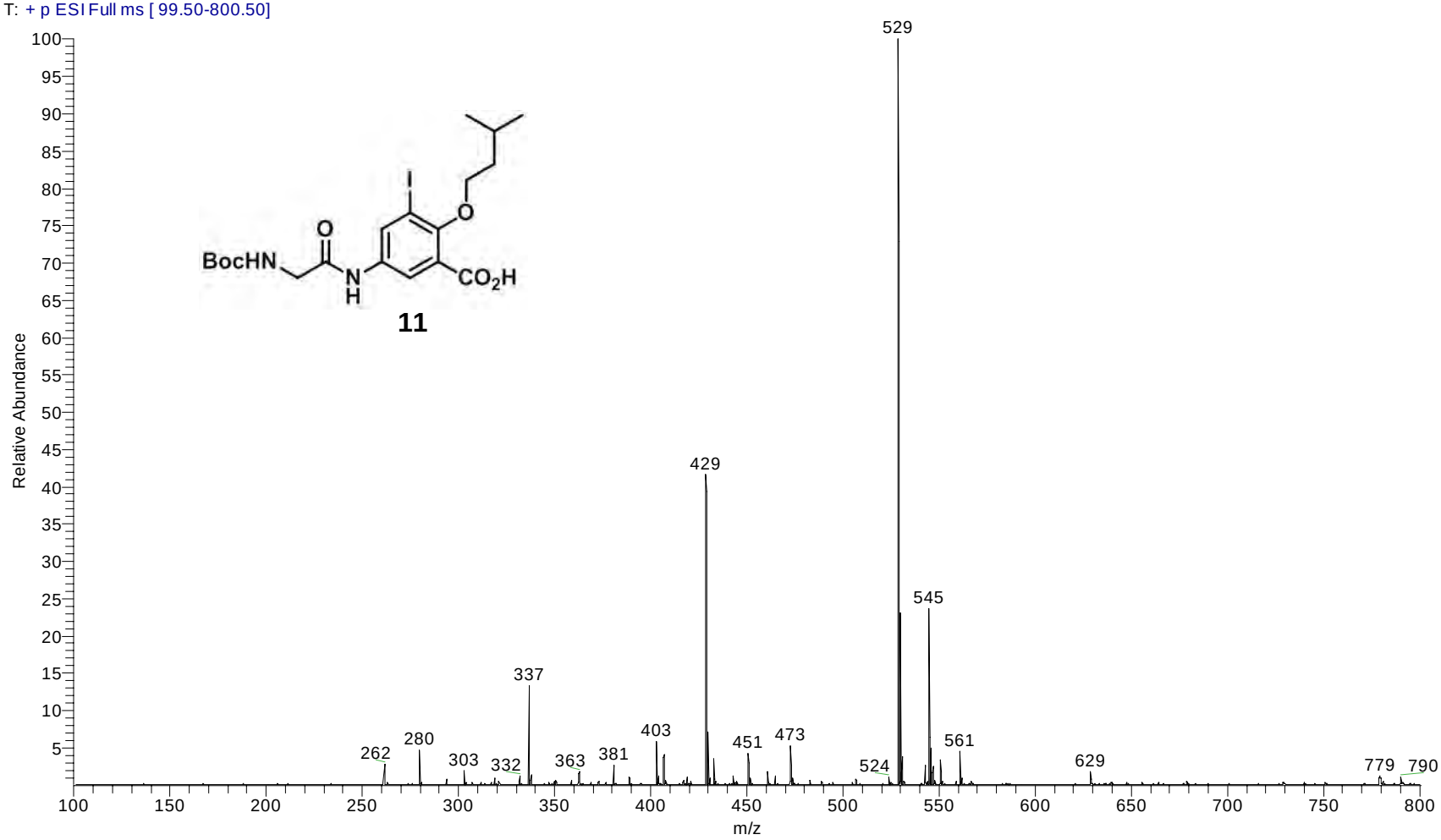
BRUKER

```
NAME          Sun-10102013-(I)-BOC-COOH
EXPNO                    1
PROCNO                   1
Date_             20131010
Time                 15.01
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG               zg30
TD                   32768
SOLVENT                MeOD
NS                       16
DS                        2
SWH               8223.685 Hz
FIDRES            0.250967 Hz
AQ                1.9923444 sec
RG                       8
DW                  60.800 usec
DE                   6.50 usec
TE                  295.9 K
D1                1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.00 usec
PL1                   1.00 dB
PL1W            13.56617069 W
SFO1           400.1924713 MHz
SI                   32768
SF             400.1900132 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

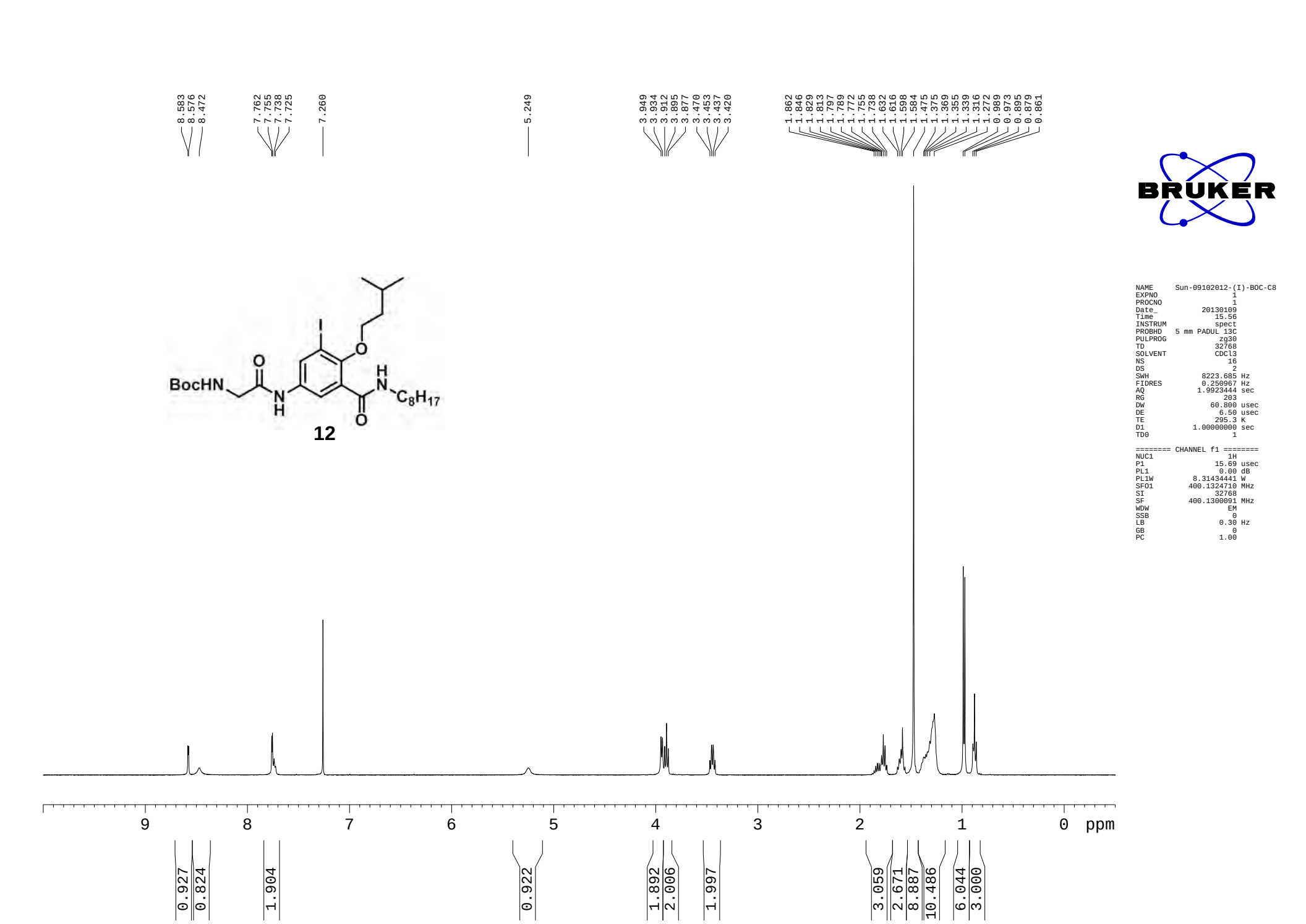

170.569
170.198
158.376
154.620
136.161
134.031
129.962
123.287
93.902
80.600
74.466
49.639
49.427
49.213
49.000
48.787
48.575
48.362
44.984
39.939
28.572
25.786
23.044
BocHN
O
N
H
O
I
CO2H
11
NAME Sun-10102013-(I)-BOC-COOH
EXPNO 2
PROCNO 1
Date_ 20131010
Time 14.49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 217
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1820
DW 20.800 usec
DE 6.50 usec
TE 296.0 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6277392 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

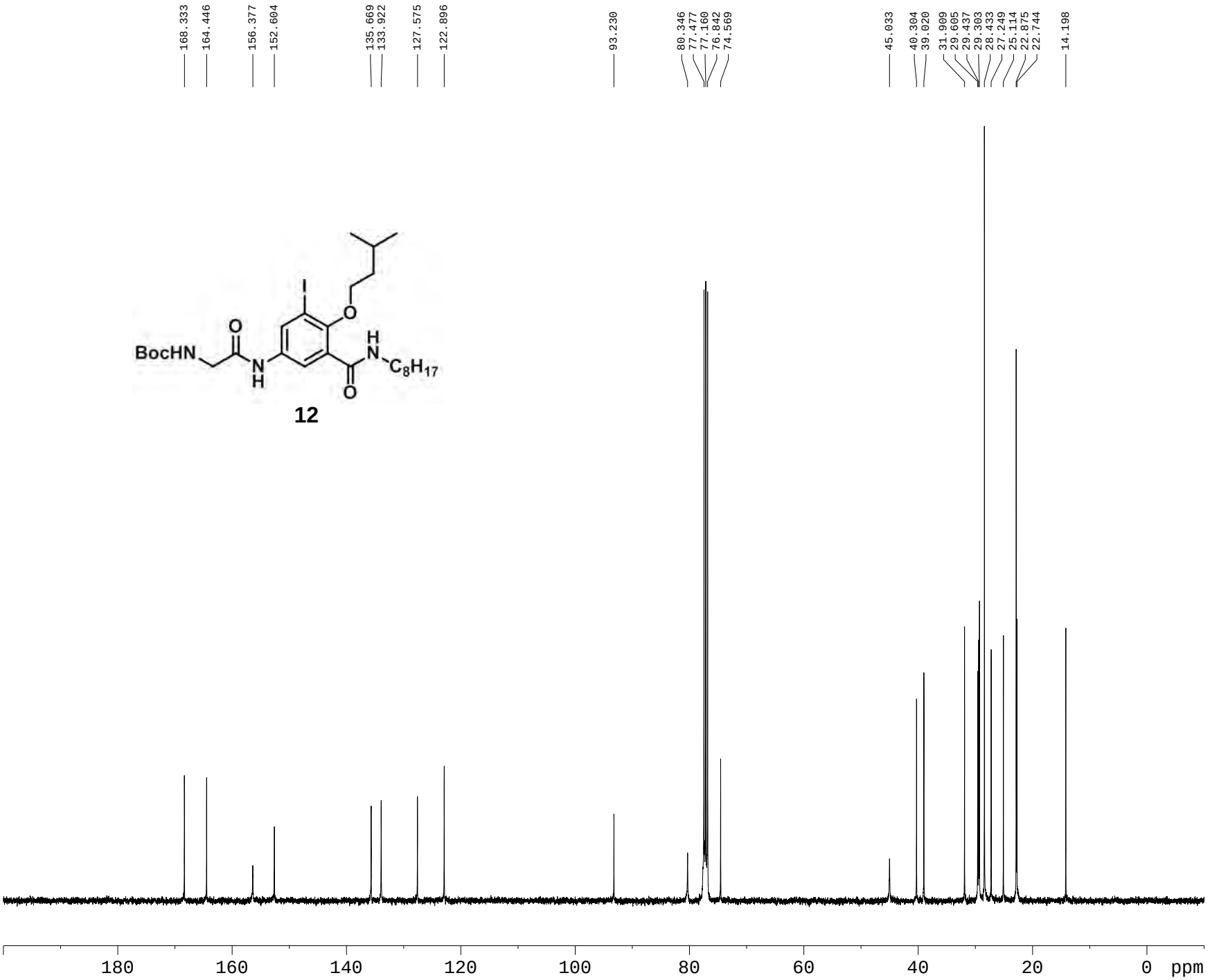
D:\MS_raw_data\hfc2021 10/23/13 04:03:05 PM (I,ic5)-BOC-COOH
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

hfc2021 #1-2 RT: 0.15-0.23 AV: 2 SM: 5G NL: 7.96E5
T: + p ESI Full ms [99.50-800.50]



11


8.583
8.576
8.472
7.762
7.755
7.738
7.725
7.260
5.249
3.949
3.934
3.912
3.895
3.877
3.470
3.453
3.437
3.420
1.862
1.846
1.829
1.813
1.797
1.789
1.772
1.755
1.738
1.632
1.616
1.598
1.584
1.475
1.375
1.369
1.355
1.339
1.316
1.272
0.989
0.973
0.895
0.879
0.861
BocHN
O
N
H
I
O
H
N
C8H17
O
12
BRUKER
NAME Sun-09102012-(I)-BOC-C8
EXPNO 1
PROCNO 1
Date_ 20130109
Time 15.56
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 295.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.69 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
0.927
0.824
1.904
0.922
1.892
2.006
1.997
3.059
2.671
8.887
10.486
6.044
3.000

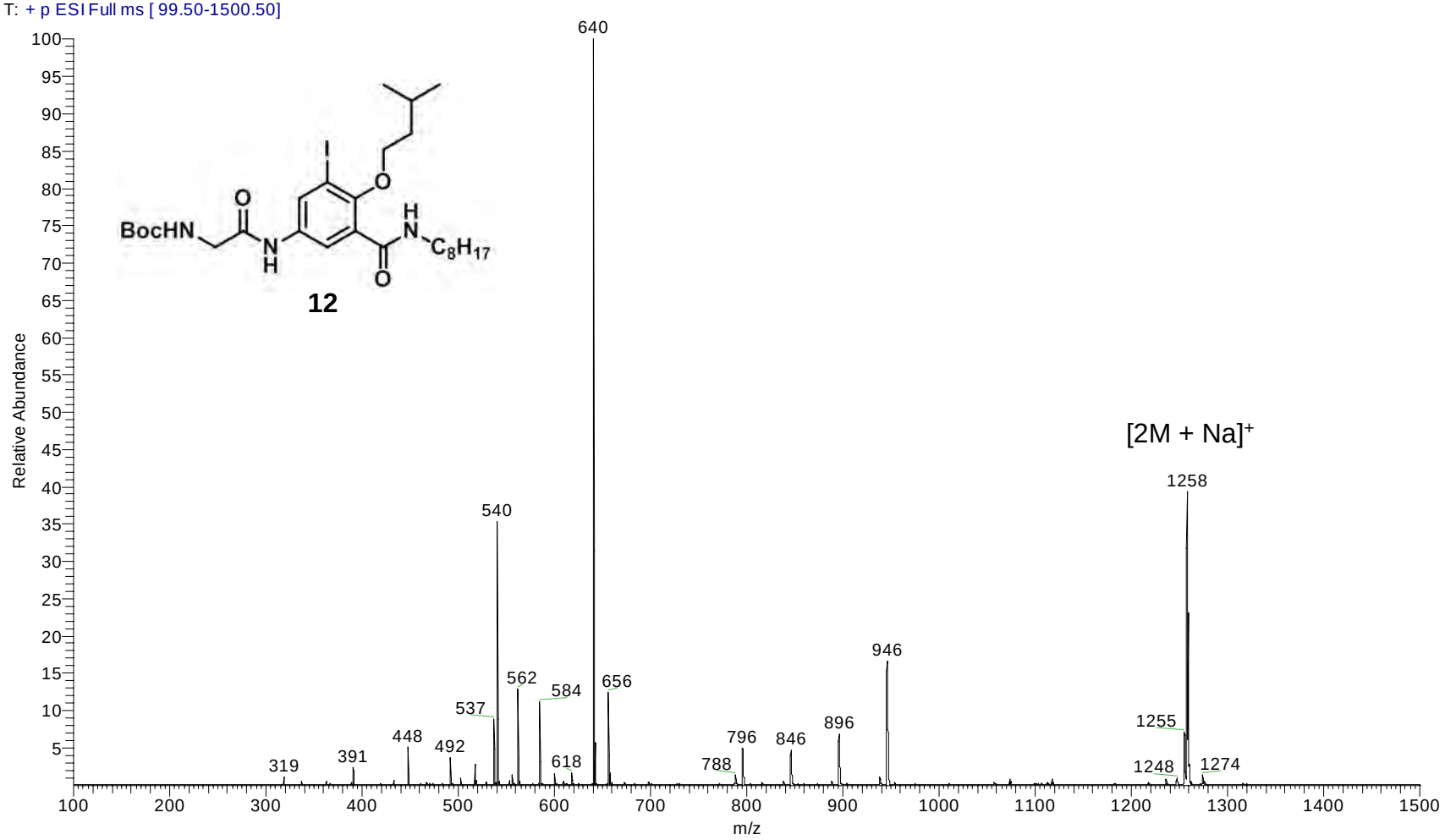


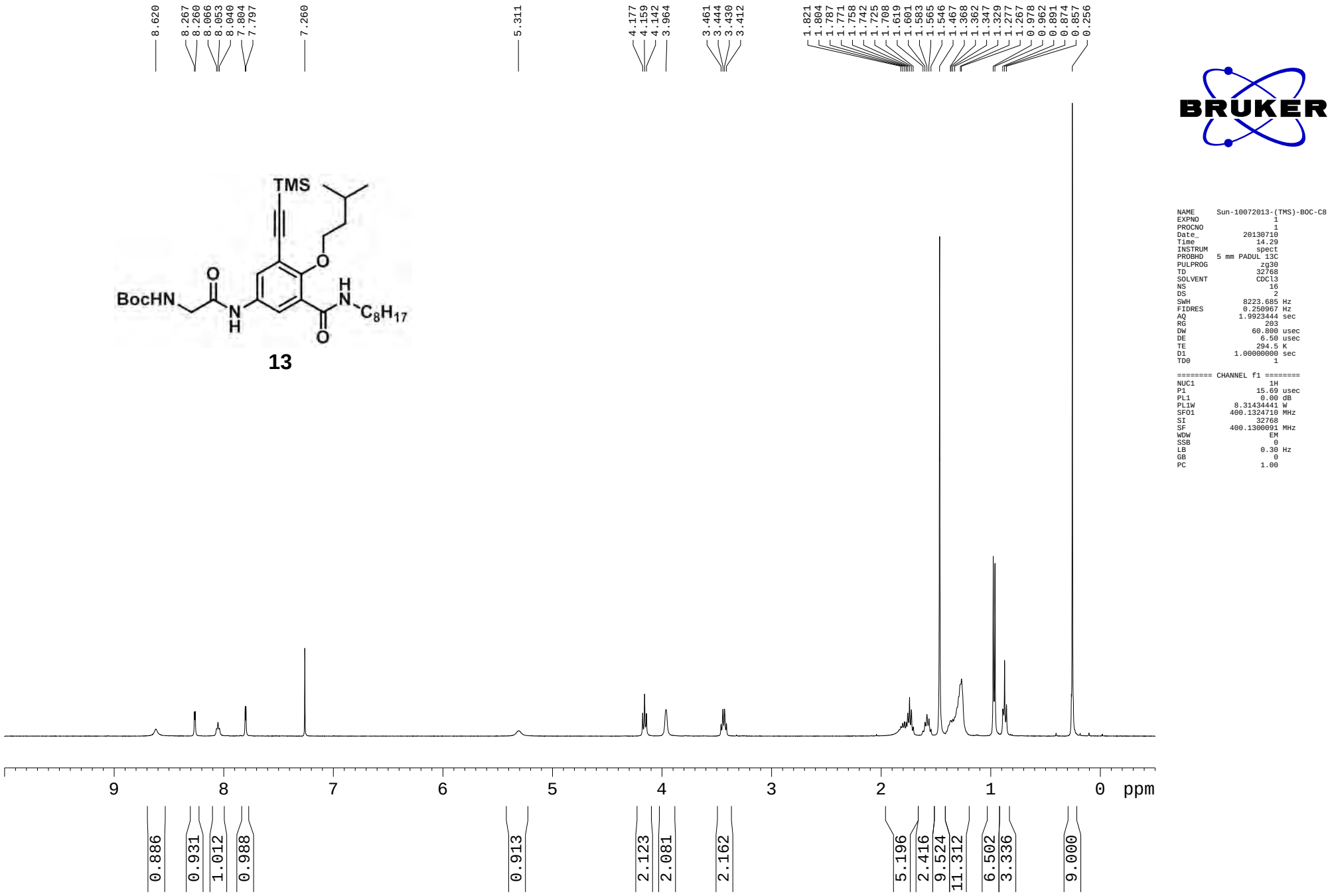
BRUKER

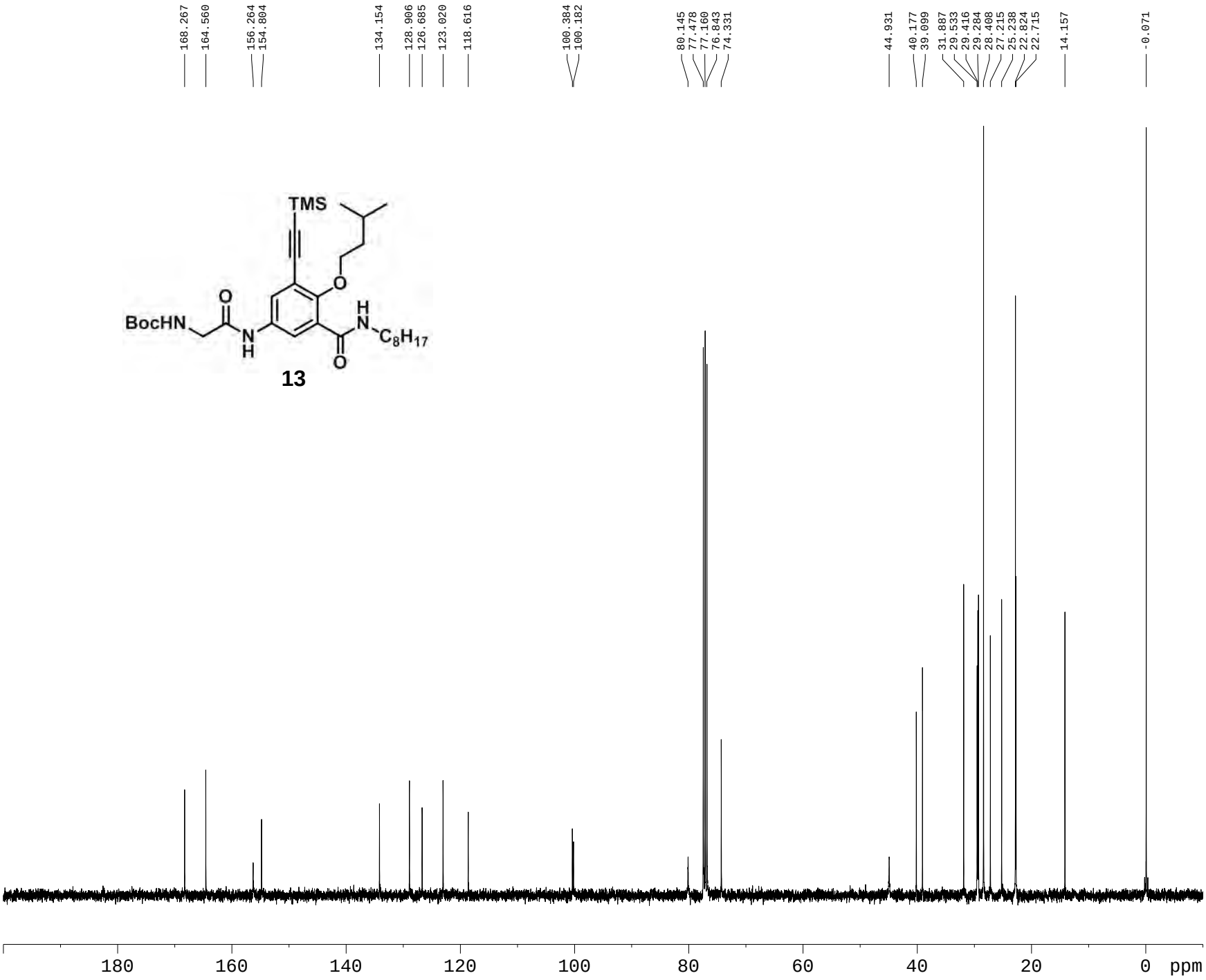
```
NAME          Sun-09102012-(I)-BOC-C8
EXPNO                              2
PROCNO                             1
Date_                       20120921
Time                           10.04
INSTRUM                        spect
PROBHD     5 mm PABBI 1H/
PULPROG                     zgpg30
TD                              65536
SOLVENT                       CDCl3
NS                               3329
DS                                  4
SWH                     24038.461 Hz
FIDRES                   0.366798 Hz
AQ                       1.3631988 sec
RG                             203
DW                           20.800 usec
DE                            6.50 usec
TE                           294.8 K
D1                    2.00000000 sec
D11                   0.03000000 sec
TD0                                1

======== CHANNEL f1 ========
NUC1                          13C
P1                          14.50 usec
PL1                          -4.00 dB
PL1W                 90.22689819 W
SFO1                100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                   waltz16
NUC2                          1H
PCPD2                       90.00 usec
PL2                          -2.00 dB
PL12                         20.06 dB
PL13                         22.00 dB
PL2W                13.17734718 W
PL12W                0.08200268 W
PL13W                0.05245997 W
SFO2                400.1316005 MHz
SI                           32768
SF                  100.6127506 MHz
WDW                             EM
SSB                              0
LB                           1.00 Hz
GB                               0
PC                           1.40
```

D:\MS_raw_data\hfc1506_120828120353 08/28/12 12:03:53 PM (I,ic5)-Boc-C8
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

hfc1506_120828120353 #1-3 RT: 0.12-0.29 AV: 3 SM: 5G NL: 1.43E6
T: + p ESI Full ms [99.50-1500.50]




8.620
8.267
8.260
8.066
8.053
8.040
7.804
7.797
7.260
5.311
4.177
4.159
4.142
3.964
3.461
3.444
3.430
3.412
1.821
1.804
1.787
1.771
1.758
1.742
1.725
1.708
1.619
1.601
1.583
1.565
1.546
1.467
1.368
1.362
1.347
1.329
1.277
1.267
0.978
0.962
0.891
0.874
0.857
0.256
TMS
BocHN
O
N
H
O
O
H
N
C8H17
O
13
NAME Sun-10072013-(TMS)-BOC-C8
EXPNO 1
PROCNO 1
Date_ 20130710
Time 14.29
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 294.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.69 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
0.886
0.931
1.012
0.988
0.913
2.123
2.081
2.162
5.196
2.416
9.524
11.312
6.502
3.336
9.000

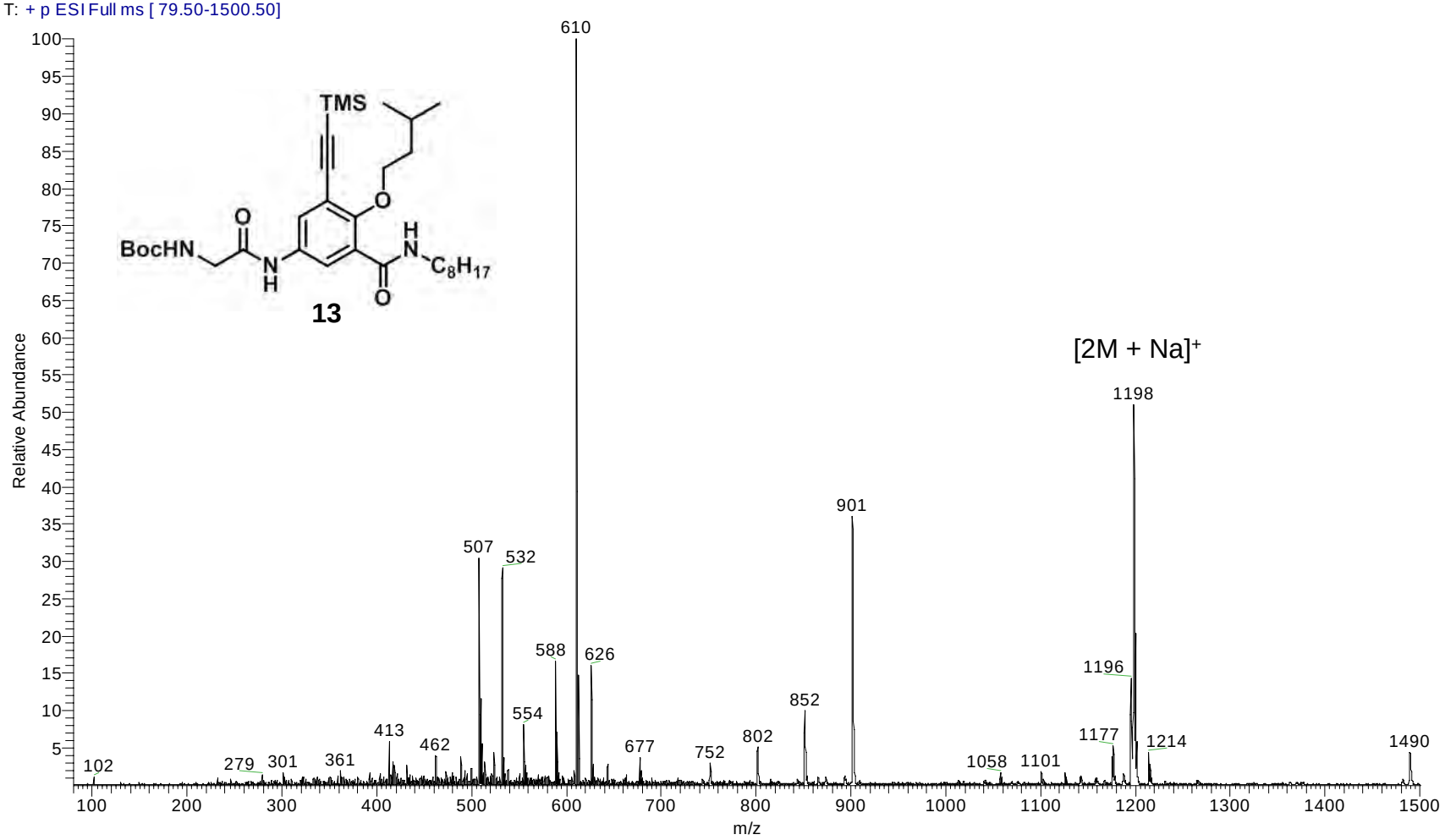


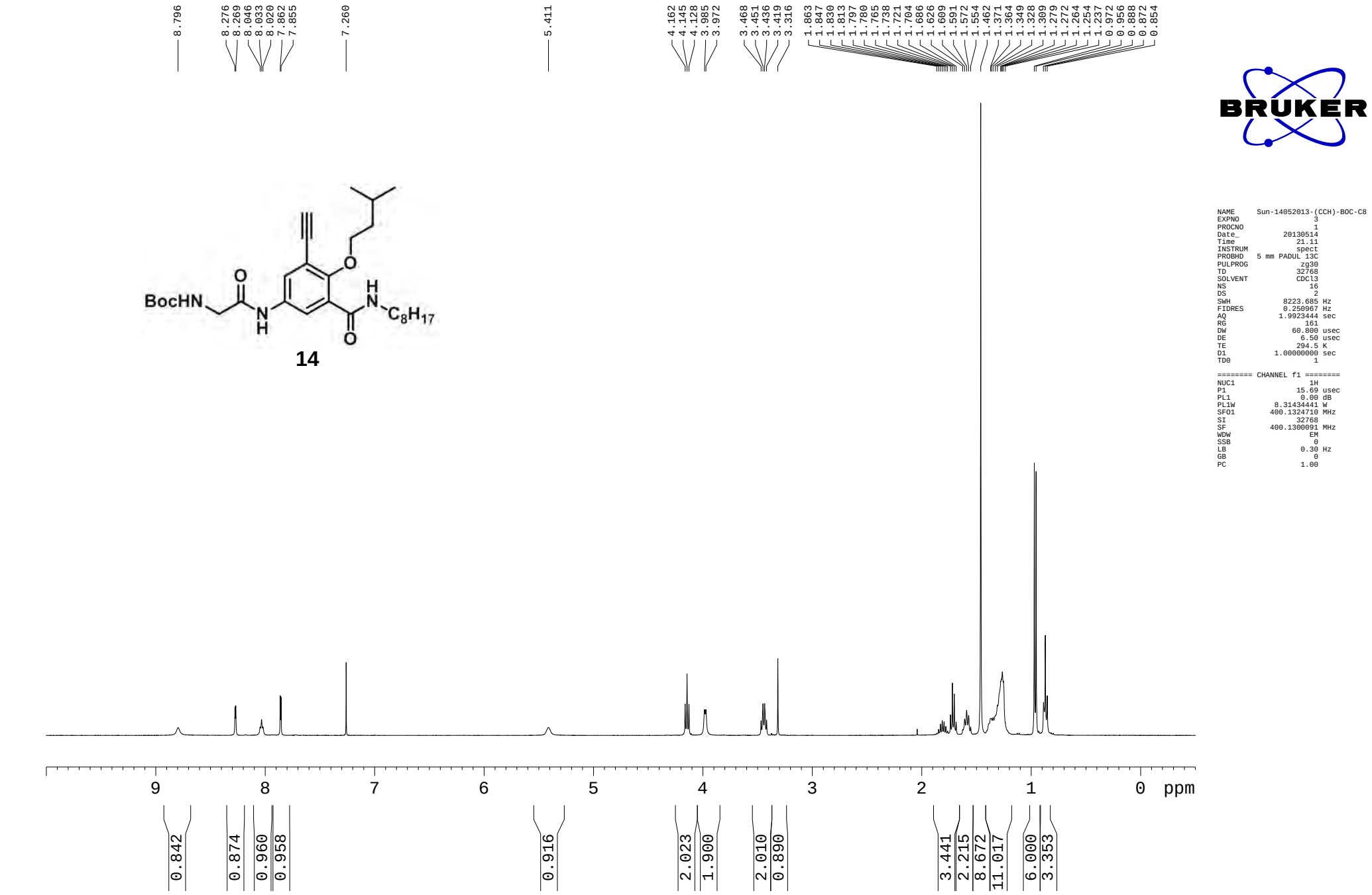
BRUKER

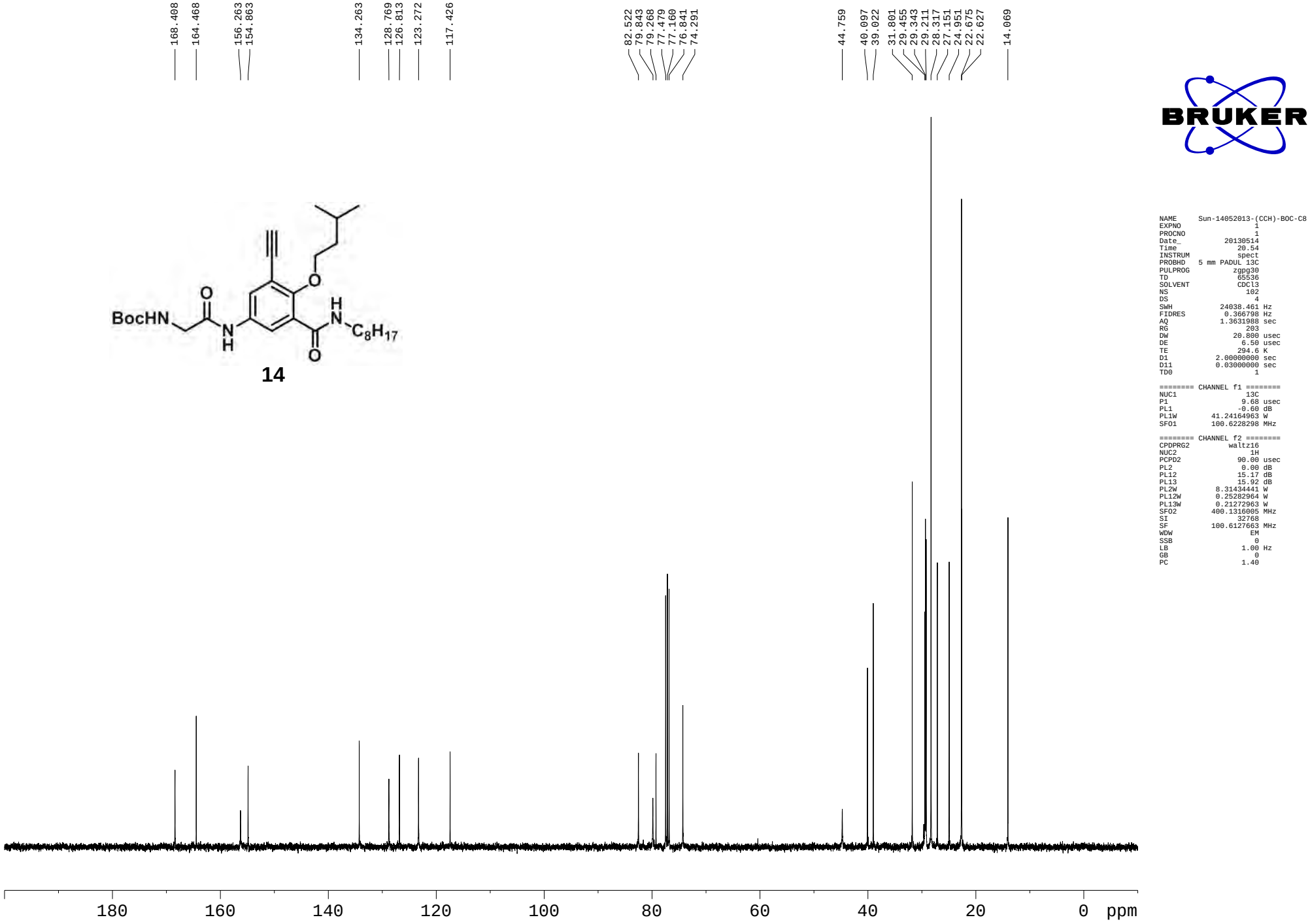
```
NAME          Sun-10072013-(TMS)-BOC-C8
EXPNO                                 2
PROCNO                                1
Date_                          20130711
Time                              11.57
INSTRUM                           spect
PROBHD     5 mm PADUL 13C
PULPROG                        zgpg30
TD                                65536
SOLVENT                        CDCl3
NS                                  170
DS                                    4
SWH                        24038.461 Hz
FIDRES                      0.366798 Hz
AQ                          1.3631988 sec
RG                                  203
DW                             20.800 usec
DE                              6.50 usec
TE                              294.7 K
D1                         2.00000000 sec
D11                        0.03000000 sec
TD0                                   1

======== CHANNEL f1 ========
NUC1                              13C
P1                              9.68 usec
PL1                            -0.60 dB
PL1W                    41.24164963 W
SFO1                    100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                     waltz16
NUC2                              1H
PCPD2                          90.00 usec
PL2                             0.00 dB
PL12                           15.17 dB
PL13                           15.92 dB
PL2W                     8.31434441 W
PL12W                    0.25282964 W
PL13W                    0.21272963 W
SFO2                    400.1316005 MHz
SI                             32768
SF                      100.6127599 MHz
WDW                               EM
SSB                                0
LB                              1.00 Hz
GB                                 0
PC                              1.40
```

D:\MS_raw_data\hfc1528 11/27/12 02:49:54 PM (TMS,ic5)-BOC-C8
esi pos, 3kv, 15ul/min, w/ sheath gas, unknown conc.

hfc1528 #2-4 RT: 0.22-0.38 AV: 3 SM: 5G NL: 8.28E5
T: + p ESI Full ms [79.50-1500.50]




8.796
8.276
8.269
8.046
8.033
8.020
7.862
7.855
7.260
5.411
4.162
4.145
4.128
3.985
3.972
3.468
3.451
3.436
3.419
3.316
1.863
1.847
1.830
1.813
1.797
1.780
1.765
1.738
1.721
1.704
1.686
1.626
1.609
1.591
1.572
1.554
1.462
1.371
1.364
1.349
1.328
1.309
1.279
1.272
1.264
1.254
1.237
0.972
0.956
0.888
0.872
0.854
BocHN
O
N
H
O
H
N
C8H17
O
14
NAME Sun-14052013-(CCH)-BOC-C8
EXPNO 3
PROCNO 1
Date_ 20130514
Time 21.11
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 161
DW 60.800 usec
DE 6.50 usec
TE 294.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.69 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300091 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
0.842
0.874
0.960
0.958
0.916
2.023
1.900
2.010
0.890
3.441
2.215
8.672
11.017
6.000
3.353



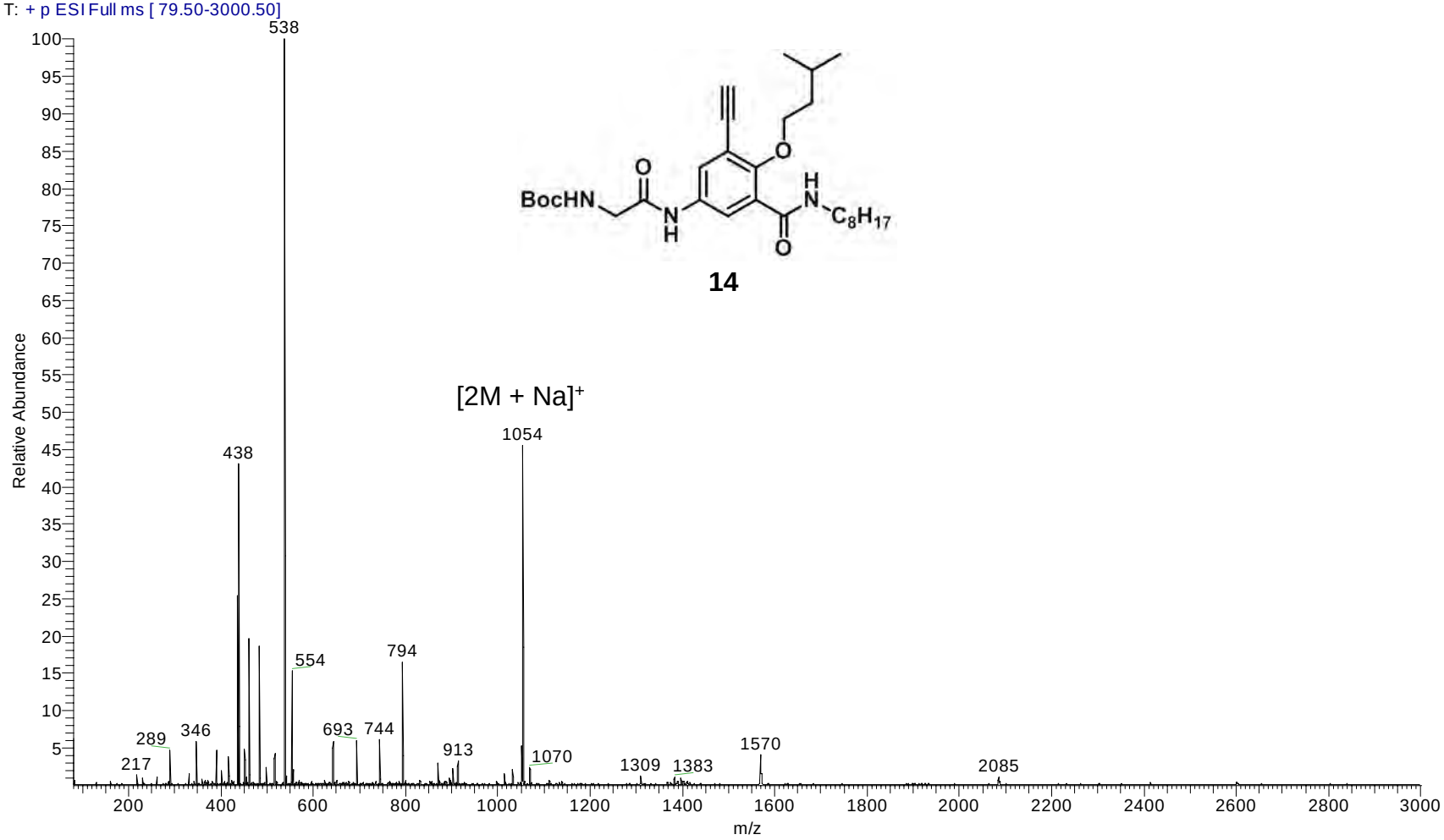
14

BRUKER

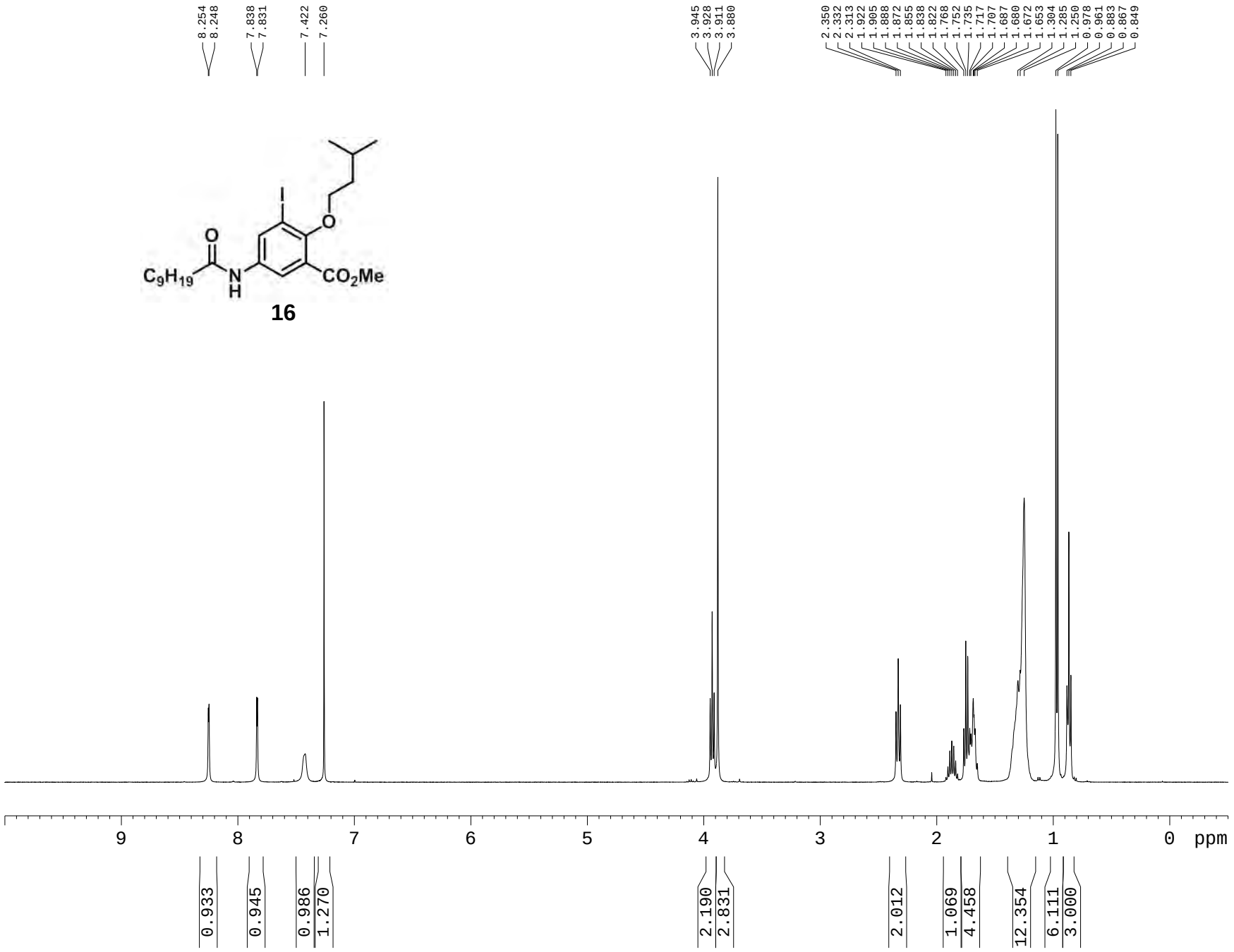
```
NAME          Sun-14052013-(CCH)-BOC-C8
EXPNO                    1
PROCNO                   1
Date_             20130514
Time                 20.54
INSTRUM              spect
PROBHD     5 mm PADUL 13C
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   102
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                   203
DW                20.800 usec
DE                 6.50 usec
TE                294.6 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                 13C
P1                 9.68 usec
PL1                -0.60 dB
PL1W        41.24164963 W
SFO1        100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2          waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2                0.00 dB
PL12              15.17 dB
PL13              15.92 dB
PL2W         8.31434441 W
PL12W        0.25282964 W
PL13W        0.21272963 W
SFO2        400.1316005 MHz
SI               32768
SF          100.6127663 MHz
WDW                 EM
SSB                  0
LB                1.00 Hz
GB                   0
PC                1.40
```

D:\MS_raw_data\hfc1529_121127153533 11/27/12 03:35:33 PM (CCH,ic5)-BOC-C8
esi pos, 3kv, 15ul/min, w/ sheath gas, unknown conc.

hfc1529_121127153533 #1-2 RT: 0.14-0.22 AV: 2 SM: 5G NL: 1.62E6
T: + p ESI Full ms [79.50-3000.50]

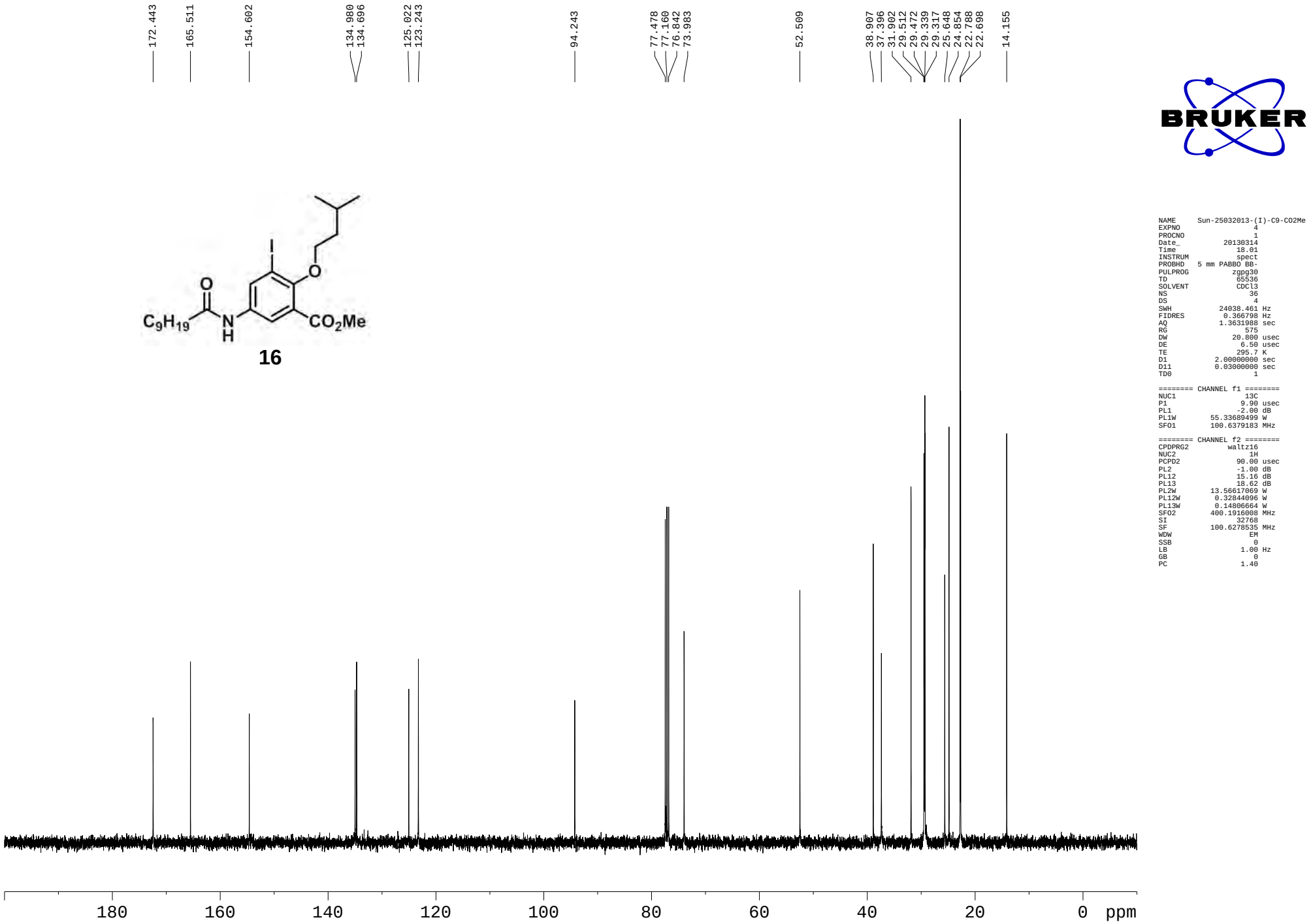


14



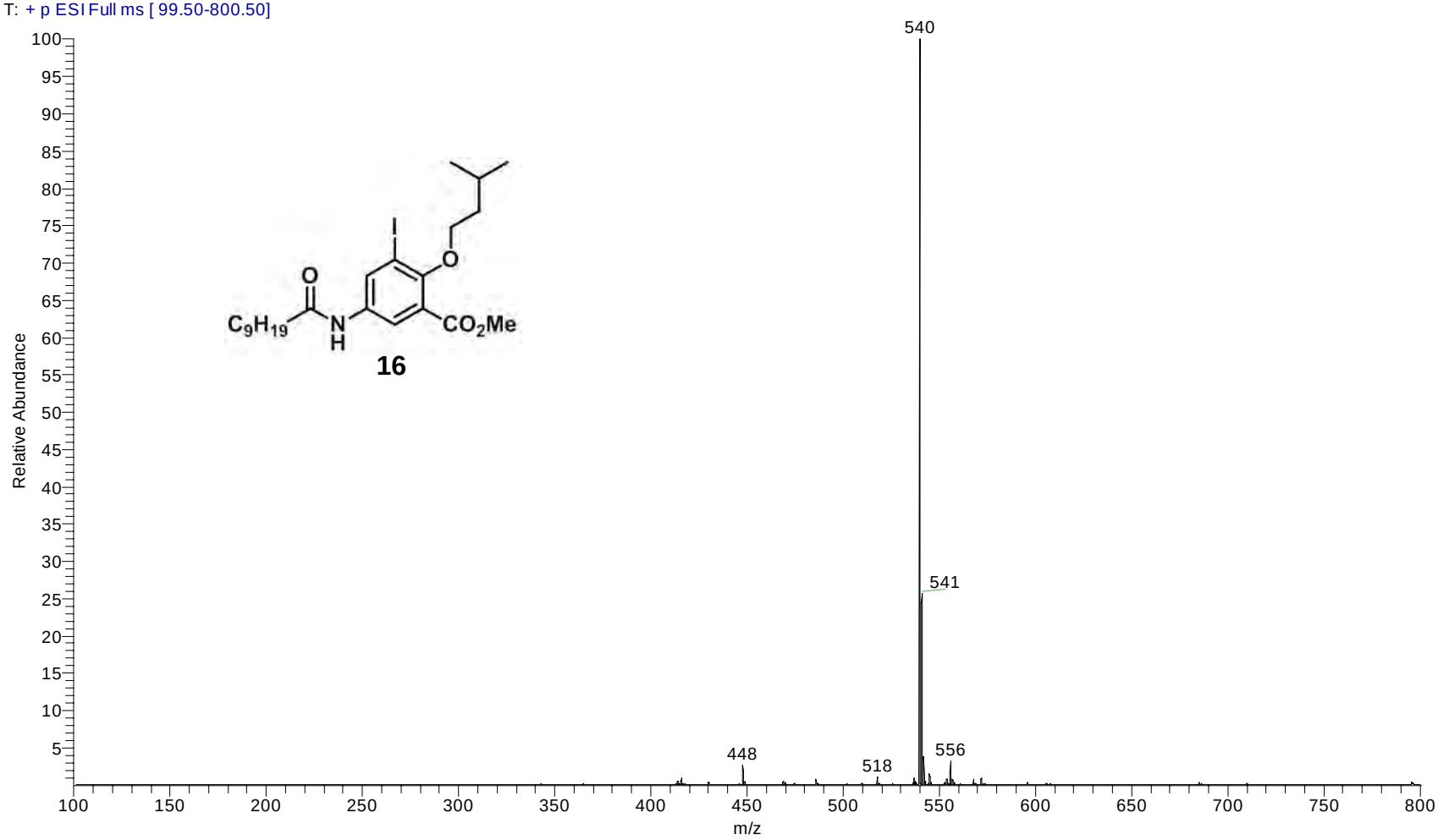
BRUKER

```
NAME        Sun-25032013-(I)-C9-CO2Me
EXPNO                1
PROCNO               1
Date_         20130325
Time             21.51
INSTRUM          spect
PROBHD   5 mm PADUL 13C
PULPROG          zg30
TD              32768
SOLVENT          CDCl3
NS                  16
DS                   2
SWH           8223.685 Hz
FIDRES        0.250967 Hz
AQ            1.9923444 sec
RG                 114
DW              60.800 usec
DE               6.50 usec
TE               294.7 K
D1            1.00000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1                1H
P1               15.69 usec
PL1               0.00 dB
PL1W        8.31434441 W
SFO1       400.1324710 MHz
SI              32768
SF         400.1300091 MHz
WDW                EM
SSB                 0
LB               0.30 Hz
GB                  0
PC               1.00
```

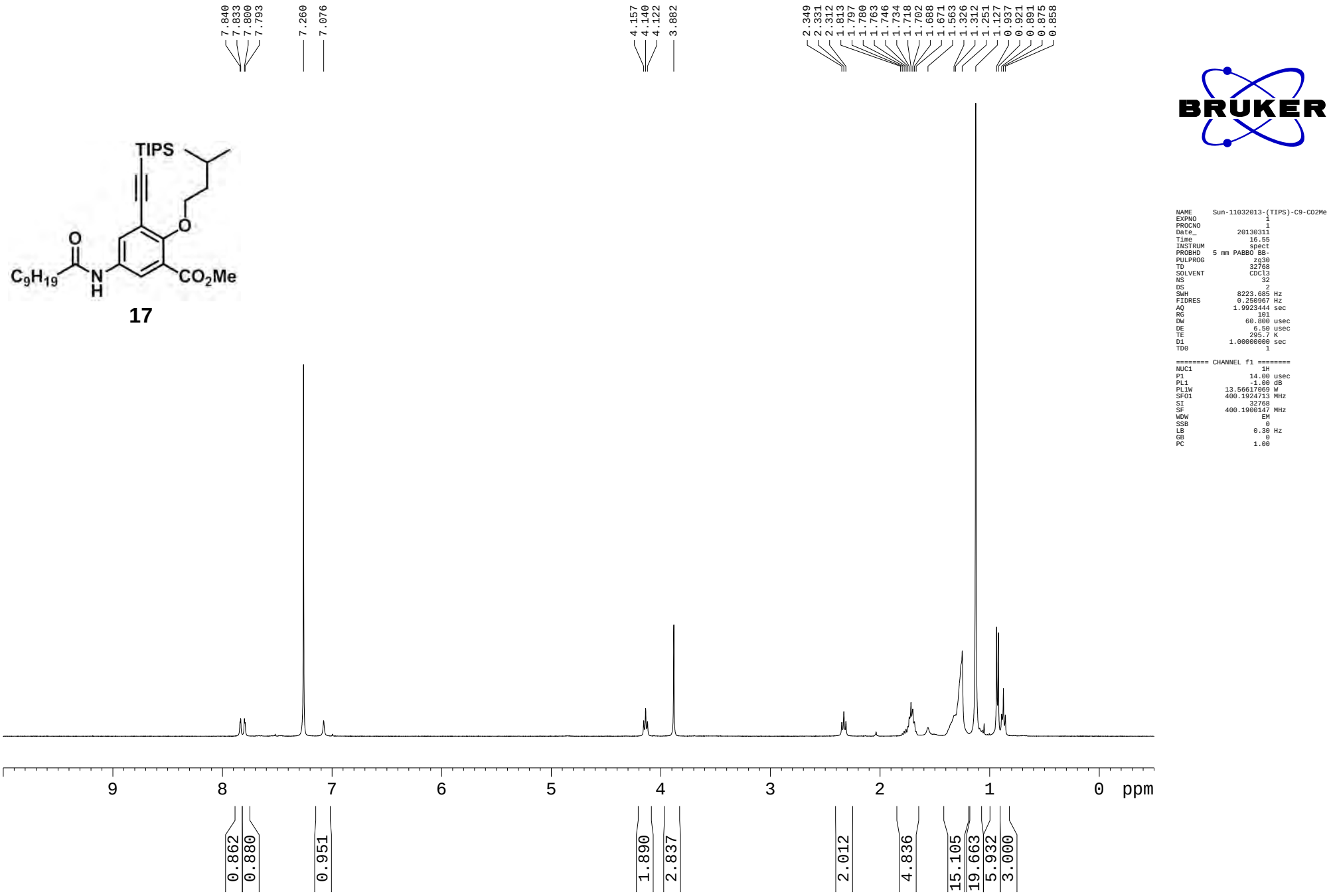

172.443
165.511
154.602
134.980
134.696
125.022
123.243
94.243
77.478
77.160
76.842
73.983
52.509
38.907
37.396
31.902
29.512
29.472
29.339
29.317
25.648
24.854
22.788
22.698
14.155
BRUKER
I
O
O
N
H
C_9H_{19}
CO_2Me
16
NAME Sun-25032013-(I)-C9-CO2Me
EXPNO 4
PROCNO 1
Date_ 20130314
Time 18.01
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 36
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 575
DW 20.800 usec
DE 6.50 usec
TE 295.7 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6278535 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

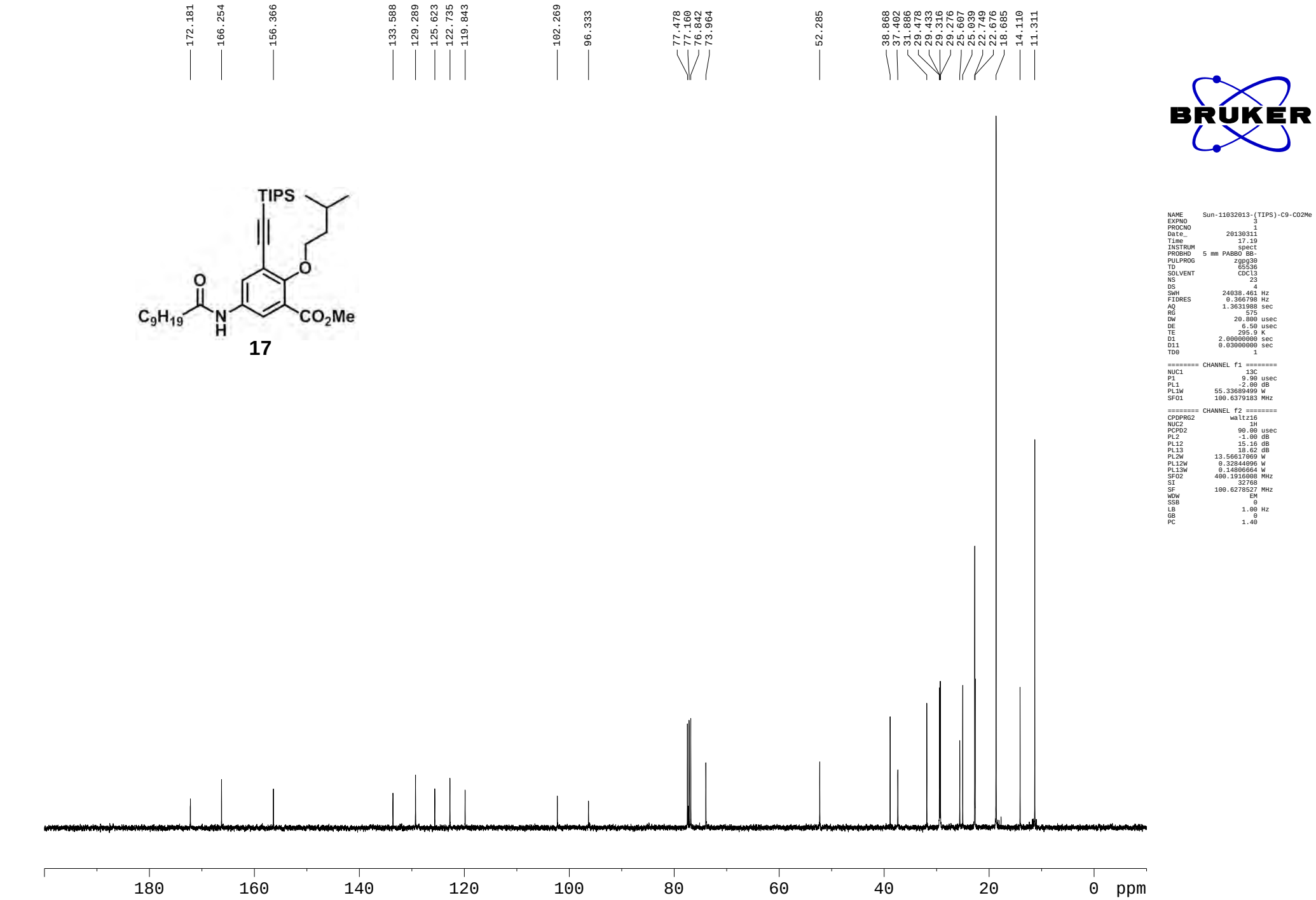
D:\MS_raw_data\hfc2007 09/24/13 04:47:36 PM (I,ic5)-C9-CO2Me
ESI pos, 3kV, 15uL/min, w/ sheath gas, unknown conc

hfc2007 #1-2 RT: 0.12-0.20 AV: 2 SM: 5G NL: 4.22E6
T: + p ESI Full ms [99.50-800.50]



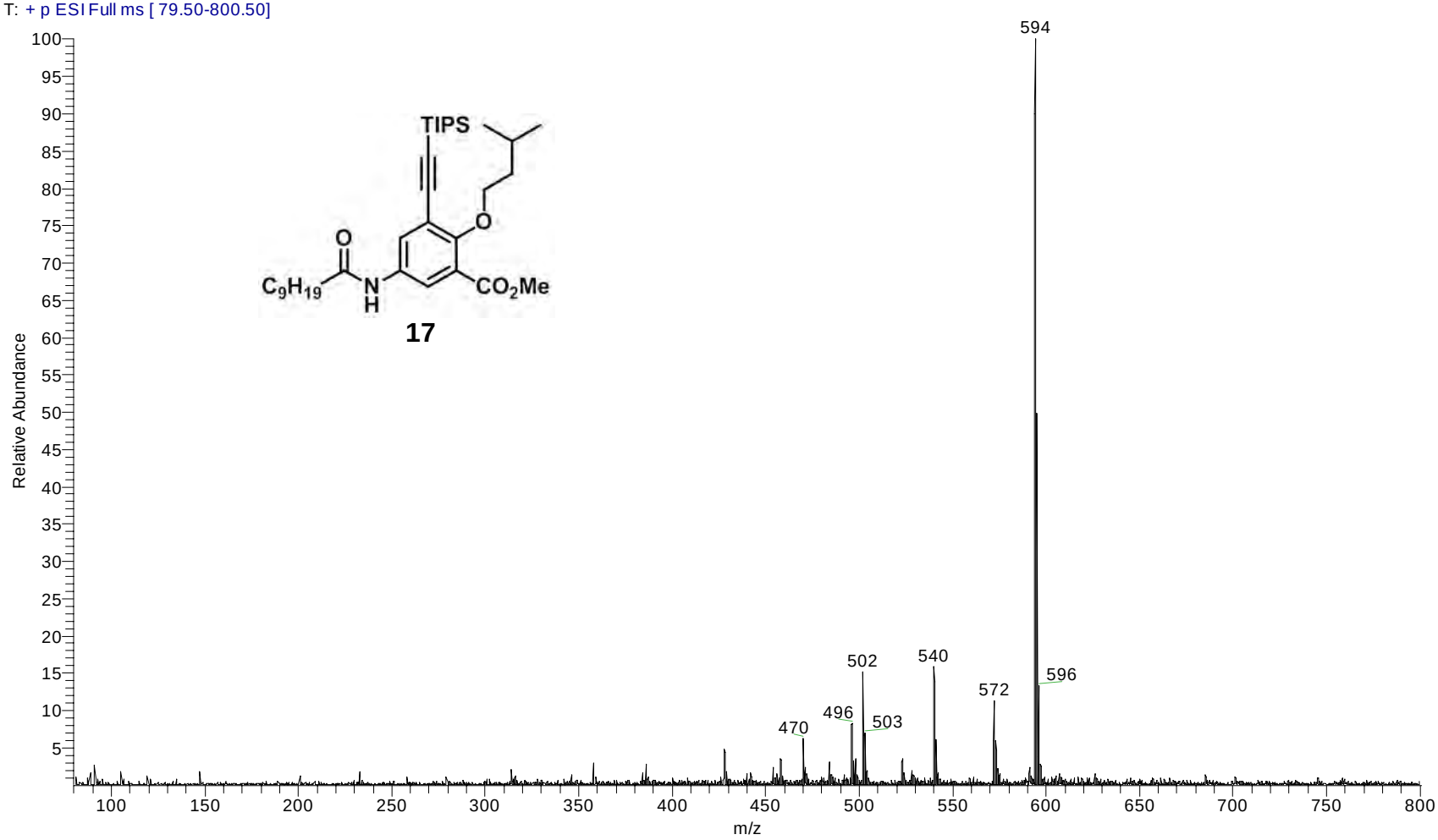
16


7.840
7.833
7.800
7.793
7.260
7.076
4.157
4.140
4.122
3.882
2.349
2.331
2.312
1.813
1.797
1.780
1.763
1.746
1.734
1.718
1.702
1.688
1.671
1.563
1.326
1.312
1.251
1.127
0.937
0.921
0.891
0.875
0.858
TIPS
O
O
N
H
C_9H_{19}
CO_2Me
17
BRUKER
NAME Sun-11032013-(TIPS)-C9-CO2Me
EXPNO 1
PROCNO 1
Date_ 20130311
Time 16.55
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 101
DW 60.800 usec
DE 6.50 usec
TE 295.7 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1900147 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
0.862
0.880
0.951
1.890
2.837
2.012
4.836
15.105
19.663
5.932
3.000

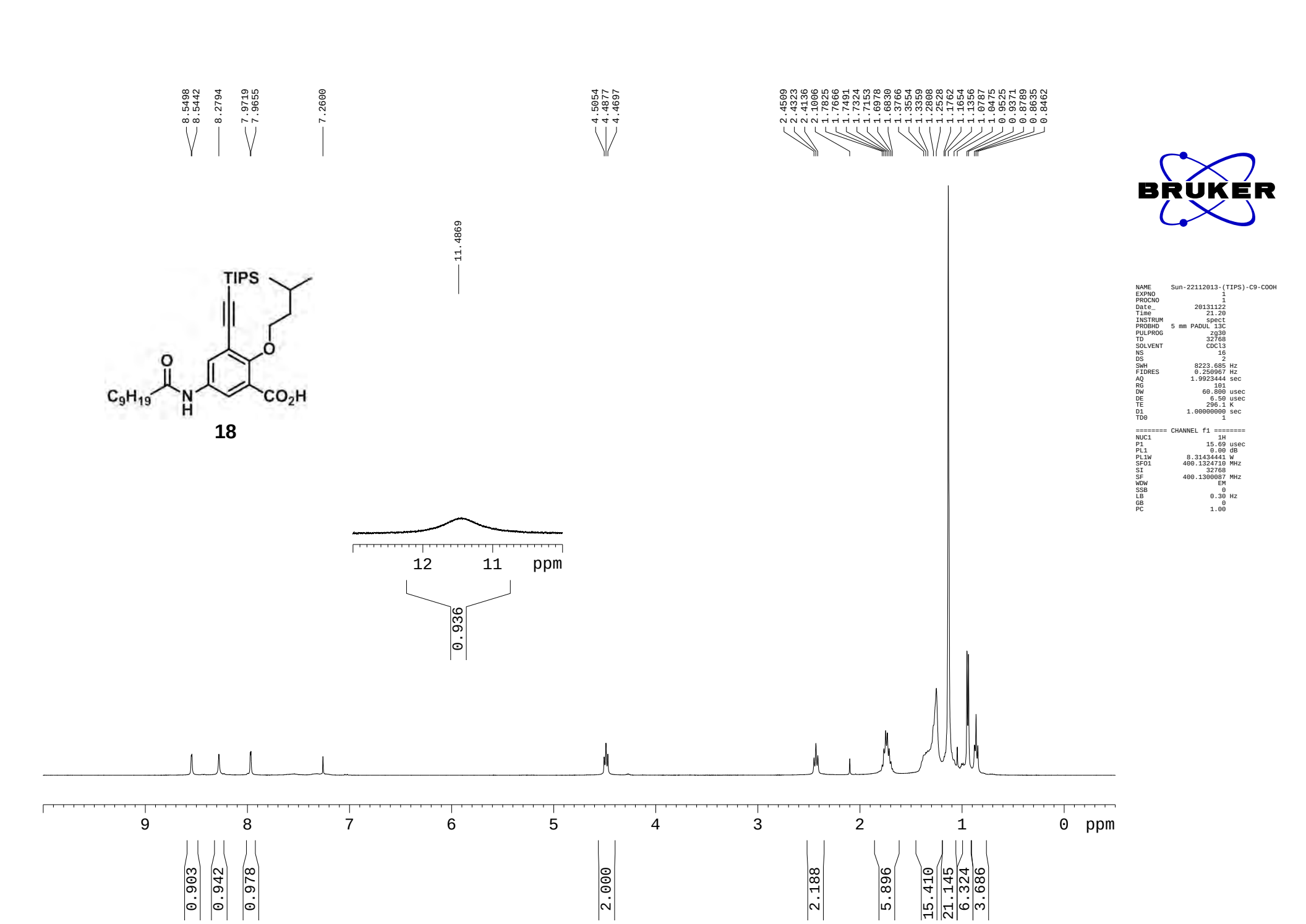

172.181
166.254
156.366
133.588
129.289
125.623
122.735
119.843
102.269
96.333
77.478
77.160
76.842
73.964
52.285
38.868
37.402
31.886
29.478
29.433
29.316
29.276
25.607
25.039
22.749
22.676
18.685
14.110
11.311
TIPS
O
O
N
H
C_9H_{19}
CO_2Me
17
NAME Sun-11032013-(TIPS)-C9-CO2Me
EXPNO 3
PROCNO 1
Date_ 20130311
Time 17.19
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 23
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 575
DW 20.800 usec
DE 6.50 usec
TE 295.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6278527 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

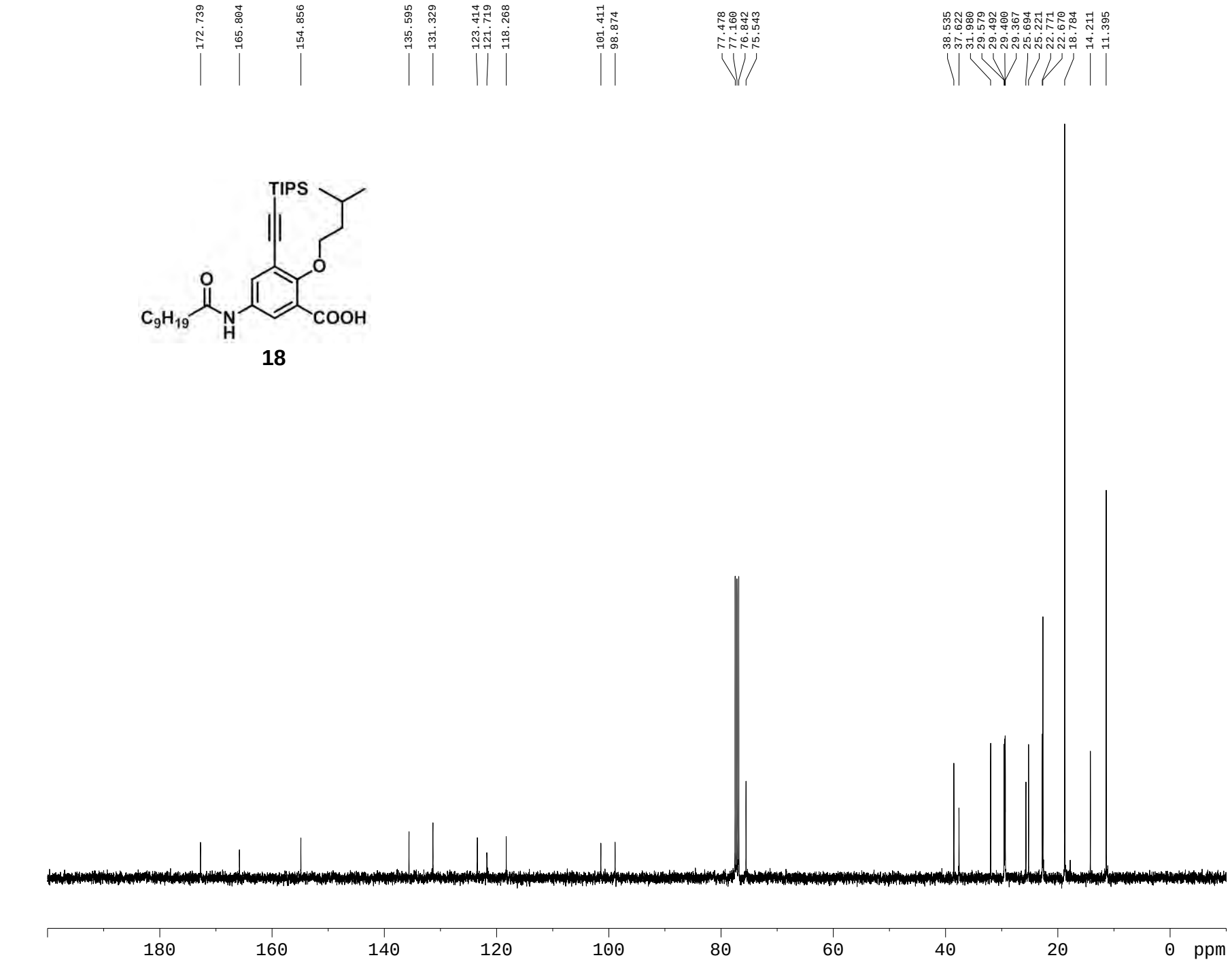
D:\MS_raw_data\hfc1583_130415142940 04/15/13 02:29:40 PM (TIPS,ic5)-C9-CO2Me
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

hfc1583_130415142940 #1-3 RT: 0.14-0.31 AV: 3 SM: 5G NL: 4.04E5
T: + p ESI Full ms [79.50-800.50]



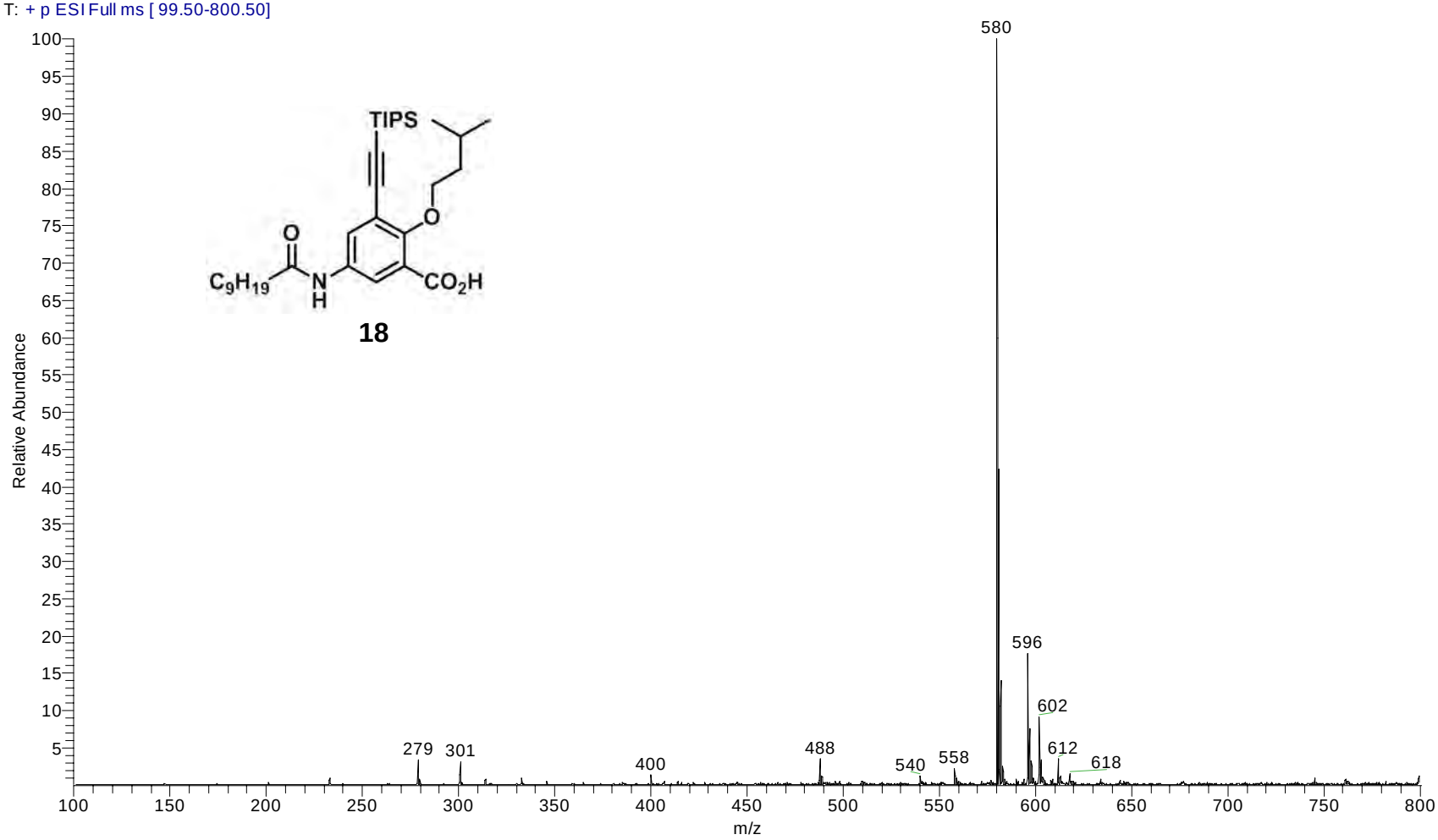
17


8.5498
8.5442
8.2794
7.9719
7.9655
7.2600
4.5054
4.4877
4.4697
2.4509
2.4323
2.4136
2.1006
1.7825
1.7666
1.7491
1.7324
1.7153
1.6978
1.6830
1.3766
1.3554
1.3359
1.2808
1.2528
1.1762
1.1654
1.1356
1.0787
1.0475
0.9525
0.9371
0.8789
0.8635
0.8462
11.4869
TIPS
O
O
N
H
C_9H_{19}
CO_2H
18
12
11
ppm
0.936
9
8
7
6
5
4
3
2
1
0
ppm
0.903
0.942
0.978
2.000
2.188
5.896
15.410
21.145
6.324
3.686
BRUKER
NAME Sun-22112013-(TIPS)-C9-COOH
EXPNO 1
PROCNO 1
Date_ 20131122
Time 21.20
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 101
DW 60.800 usec
DE 6.50 usec
TE 296.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 15.69 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

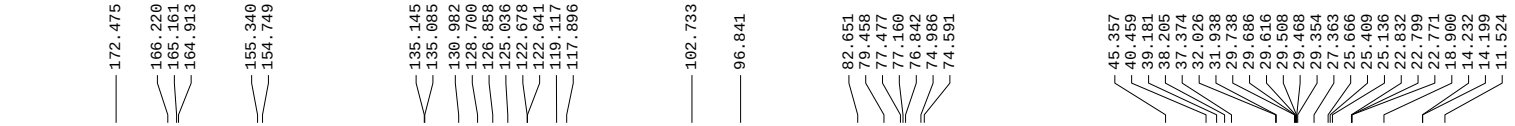

172.739
165.804
154.856
135.595
131.329
123.414
121.719
118.268
101.411
98.874
77.478
77.160
76.842
75.543
38.535
37.622
31.980
29.579
29.492
29.400
29.367
25.694
25.221
22.771
22.670
18.784
14.211
11.395
TIPS
O
O
C_9H_{19}
N
H
COOH
18
NAME Sun-22112013-(TIPS)-C9-COOH
EXPNO 2
PROCNO 1
Date_ 20131122
Time 21.33
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 65
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 296.3 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.68 usec
PL1 -9.60 dB
PL1W 41.24164963 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 15.17 dB
PL13 15.92 dB
PL2W 8.31434441 W
PL12W 0.25282964 W
PL13W 0.21272963 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127573 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

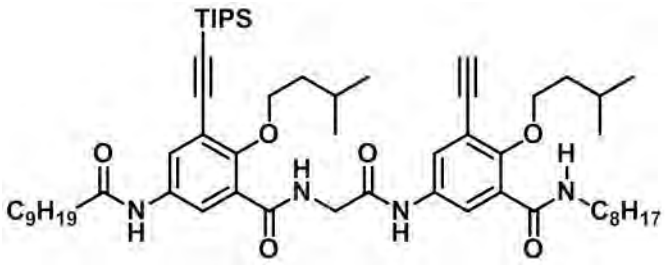
D:\MS_raw_data\hfc2020 10/23/13 03:38:00 PM (TIPS, ic5)-C9-COOH
esi pos, 3kV, 5ul/min, w/o sheath gas, unknown conc.

hfc2020 #2-4 RT: 0.22-0.38 AV: 3 SM: 5G NL: 2.42E5
T: + p ESI Full ms [99.50-800.50]



10.235
9.649
9.544
8.741
8.734
8.604
8.598
8.178
8.166
8.152
8.071
8.064
7.997
7.990
7.260
4.619
4.610
4.353
4.334
4.314
4.208
4.191
4.174
3.496
3.479
3.465
3.448
3.347
2.499
2.481
2.462
1.926
1.908
1.888
1.876
1.869
1.860
1.843
1.826
1.810
1.794
1.771
1.754
1.736
1.718
1.714
1.696
1.680
1.663
1.645
1.627
1.609
1.591
1.572
1.553
1.318
1.297
1.269
1.261
1.244
1.156
0.997
0.981
0.914
BRUKER
TIPS
C9H19
C8H17
2
NAME Sun-18032013-(TIPS,CCH)-C9-C8
EXPNO 9
PROCNO 1
Date_ 20130911
Time 22.53
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 114
DW 60.800 usec
DE 6.50 usec
TE 297.0 K
D1 2.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1900151 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0 ppm
0.984
0.908
1.019
0.958
0.930
0.993
1.004
1.013
2.024
2.036
2.039
2.017
0.969
2.000
10.025
22.992
20.511
6.468
12.233

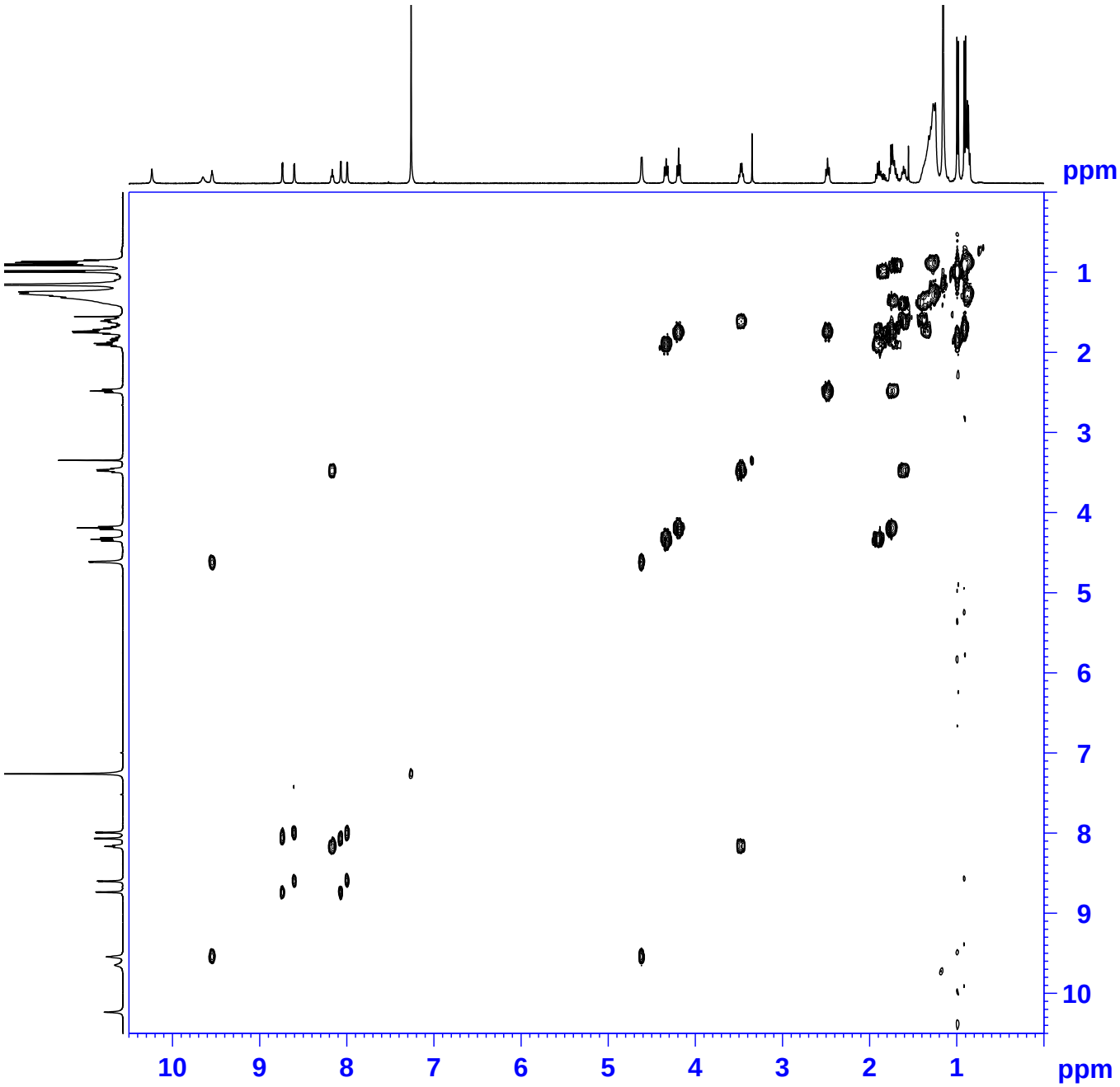




2

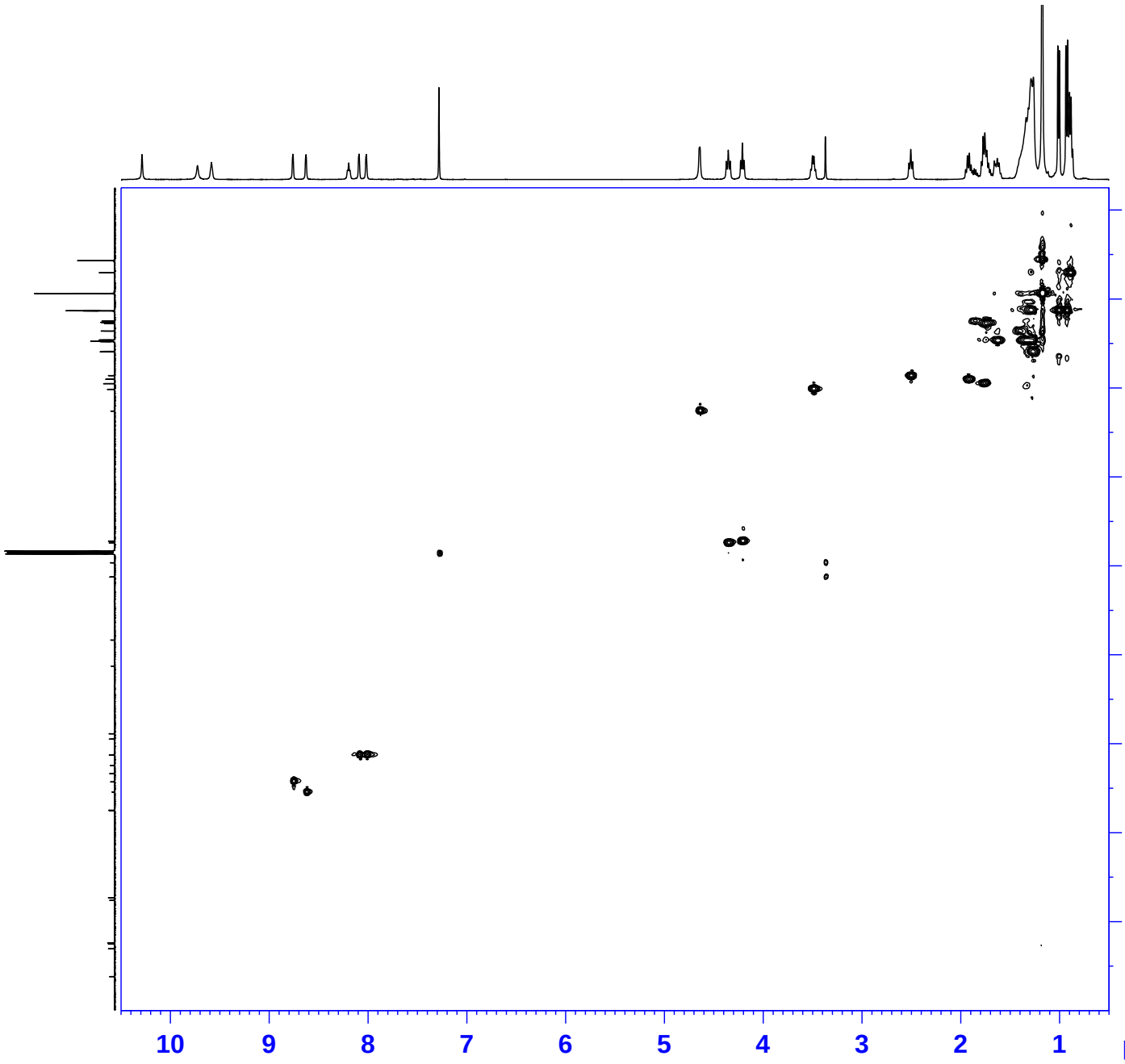
```
NAME        Sun-18032013-(TIPS,CCH)-C9-C8
EXPNO                   8
PROCNO                  1
Date_             20130319
Time                 8.30
INSTRUM             spect
PROBHD   5 mm PADUL 13C
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  4849
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   203
DW                20.800 usec
DE                 6.50 usec
TE                295.7 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.68 usec
PL1                 -0.60 dB
PL1W          41.24164963 W
SFO1         100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2               90.00 usec
PL2                  0.00 dB
PL12                15.17 dB
PL13                15.92 dB
PL2W           8.31434441 W
PL12W          0.25282964 W
PL13W          0.21272963 W
SFO2         400.1316005 MHz
SI                  32768
SF           100.6127558 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

COSY spectrum of compound **2** in $CDCl_3$ at 10 mM



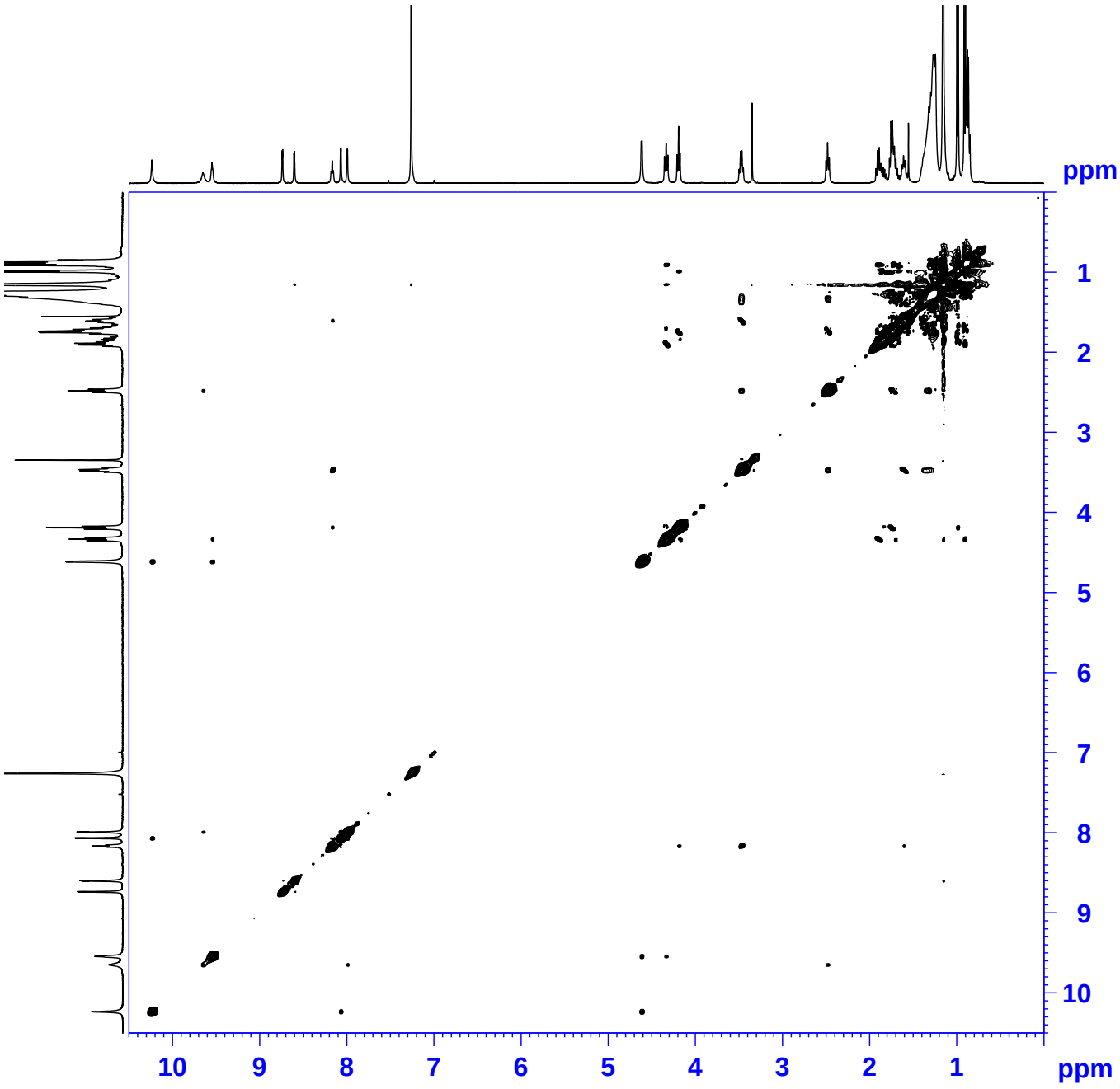

```
NAME      Sun-11092013-(TIPS,CCH)-C9-C8 10 mM
EXPNO                5
PROCNO               1
Date_         20130912
Time              4.45
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG      cosygpmfqf
TD                2048
SOLVENT           CDCl3
NS                   4
DS                   8
SWH           5341.880 Hz
FIDRES        2.608340 Hz
AQ            0.1917428 sec
RG                2050
DW               93.600 usec
DE                6.50 usec
TE                296.5 K
D0           0.00000300 sec
D1           2.00000000 sec
D13          0.00000400 sec
D16          0.00020000 sec
IN0          0.00018715 sec

======== CHANNEL f1 ========
NUC1                 1H
P1                14.00 usec
PL1               -1.00 dB
PL1W        13.56617069 W
SFO1        400.1924060 MHz

====== GRADIENT CHANNEL =====
GPNAM1          SINE.100
GPNAM2          SINE.100
GPNAM3          SINE.100
GPZ1               16.00 %
GPZ2               12.00 %
GPZ3               40.00 %
P16              1000.00 usec
ND0                   1
TD                  128
SFO1           400.1924 MHz
FIDRES        41.739697 Hz
SW               13.350 ppm
FnMODE              QF
SI                  1024
SF          400.1900132 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
PC                  1.40
SI                  1024
MC2                 QF
SF          400.1900121 MHz
WDW                 SINE
SSB                    0
LB                  0.00 Hz
GB                     0
```

HSQC spectrum of compound **2**




```
NAME      Sun-18032013-(TIPS,CCH)-C9-C8
EXPNO                7
PROCNO               1
Date_         20130319
Time              3.38
INSTRUM          spect
PROBHD   5 mm PADUL 13C
PULPROG        hsqcetgp
TD                1024
SOLVENT           CDCl3
NS                   2
DS                  16
SWH           5341.880 Hz
FIDRES        5.216680 Hz
AQ           0.0958964 sec
RG                 203
DW              93.600 usec
DE               6.50 usec
TE              294.8 K
CNST2       145.0000000
D0           0.00000300 sec
D1           1.50000000 sec
D4           0.00172414 sec
D11          0.03000000 sec
D13          0.00000400 sec
D16          0.00020000 sec
IN0          0.00002260 sec
ZGOPTNS

======== CHANNEL f1 ========
NUC1                1H
P1               15.69 usec
P2               31.38 usec
P28               0.00 usec
PL1               0.00 dB
PL1W         8.31434441 W
SFO1        400.1324057 MHz

======== CHANNEL f2 ========
CPDPRG2           garp
NUC2               13C
P3                9.68 usec
P4               19.36 usec
PCPD2            80.00 usec
PL2              -0.60 dB
PL12             17.74 dB
PL2W        41.24164963 W
PL12W        0.60441613 W
SFO2        100.6202727 MHz

====== GRADIENT CHANNEL =====
GPNAM1         SINE.100
GPNAM2         SINE.100
GPZ1             80.00 %
GPZ2             20.10 %
P16            1000.00 usec
ND0                 2
TD                256
SFO1          100.6203 MHz
FIDRES         86.470551 Hz
SW              220.000 ppm
FnMODE    Echo-Antiecho
SI                1024
SF          400.1300000 MHz
WDW               QSINE
SSB                 2
LB               0.00 Hz
GB                  0
PC                1.40
SI                1024
MC2       echo-antiecho
SF          100.6127690 MHz
WDW               QSINE
SSB                 2
LB               0.00 Hz
GB                  0
```

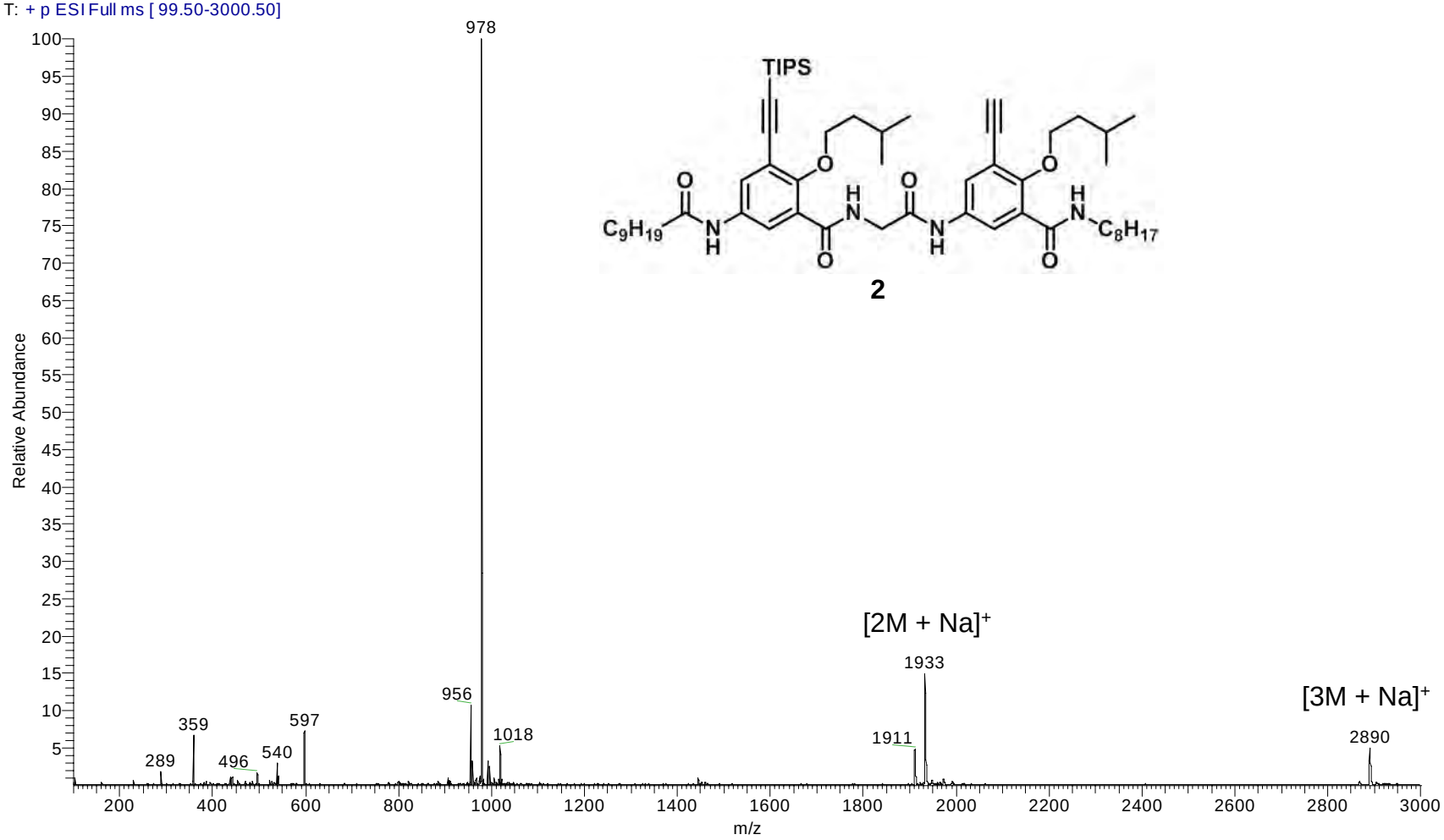
ROESY spectrum of compound **2** in $CDCl_3$ at 10 mM

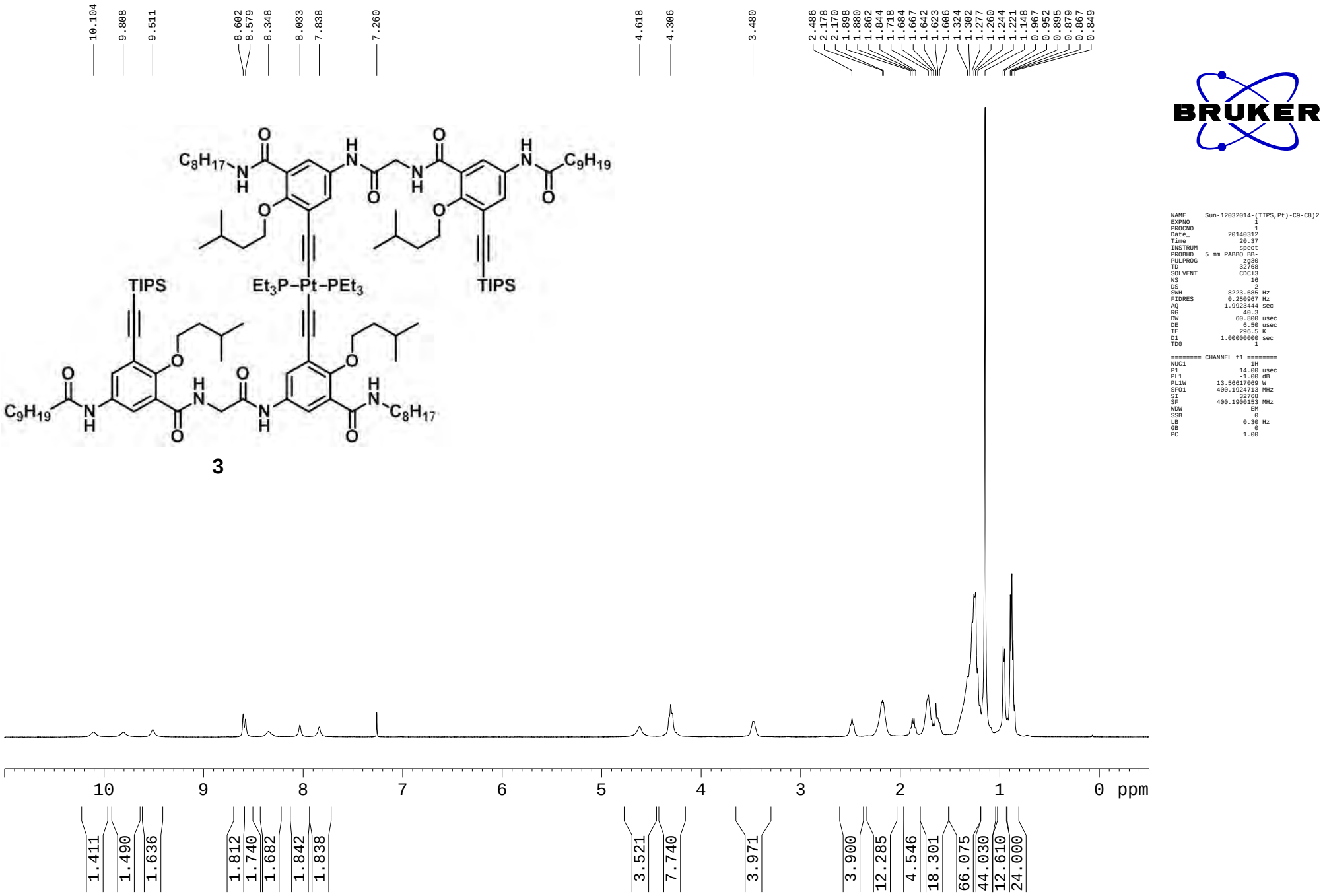


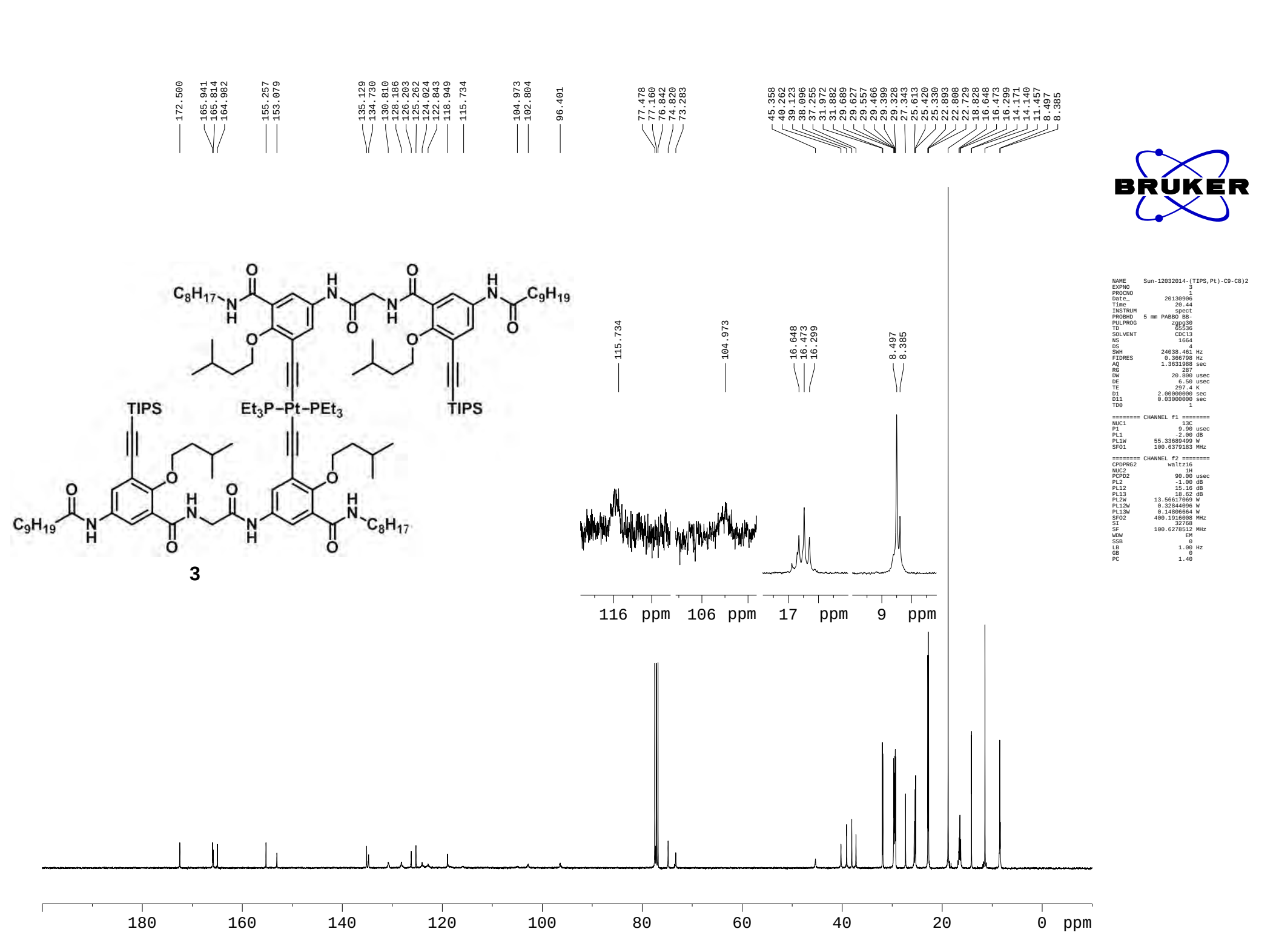

```
NAME        Sun-11092013-(TIPS,CCH)-C9-C8 10 mM
EXPNO                    3
PROCNO                   1
Date_             20130911
Time                 23.02
INSTRUM              spect
PROBHD    5 mm PABBO BB-
PULPROG            roesyph
TD                    2048
SOLVENT              CDCl3
NS                      16
DS                       4
SWH               4391.101 Hz
FIDRES            2.144092 Hz
AQ                0.2332489 sec
RG                      287
DW                 113.867 usec
DE                   6.50 usec
TE                   296.8 K
D0              0.00010095 sec
D1              2.00000000 sec
D12             0.00002000 sec
IN0             0.00022775 sec

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.00 usec
P15                200000.00 usec
PL1                  -1.00 dB
PL11                 18.02 dB
PL1W            13.56617069 W
PL11W            0.17000327 W
SFO1            400.1922156 MHz
ND0                      1
TD                     256
SFO1              400.1922 MHz
FIDRES           17.152769 Hz
SW                  10.973 ppm
FnMODE          States-TPPI
SI                    1024
SF              400.1900153 MHz
WDW                  QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
PC                    1.00
SI                    1024
MC2             States-TPPI
SF              400.1900124 MHz
WDW                  QSINE
SSB                      2
LB                    0.00 Hz
GB                       0
```

D:\MS_raw_data\hfc1585 04/16/13 05:07:29 PM (TIPS,CCH)-C9-C8
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

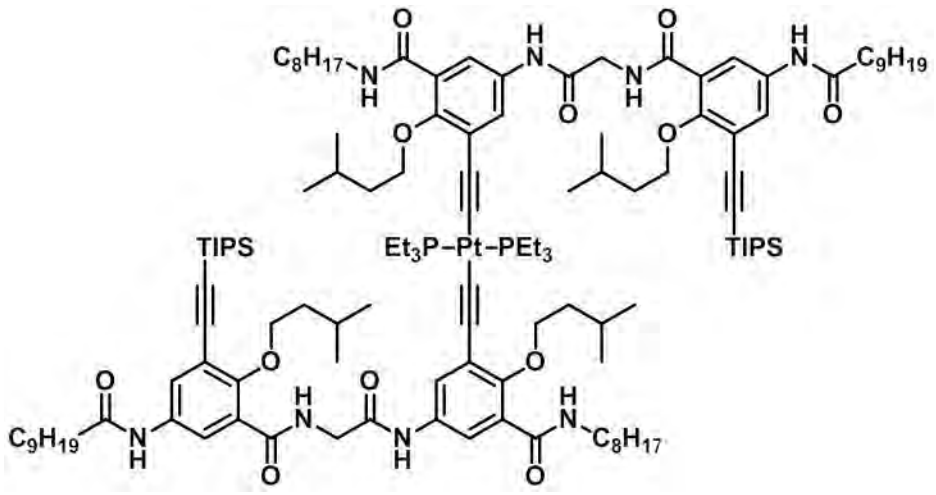
hfc1585 #1-4 RT: 0.13-0.36 AV: 4 SM: 5G NL: 2.04E6
T: + p ESI Full ms [99.50-3000.50]




10.104
9.808
9.511
8.602
8.579
8.348
8.033
7.838
7.260
4.618
4.306
3.480
2.486
2.178
2.170
1.898
1.880
1.862
1.844
1.718
1.684
1.667
1.642
1.623
1.606
1.324
1.302
1.277
1.260
1.244
1.221
1.148
0.967
0.952
0.895
0.879
0.867
0.849
TIPS
Et3P–Pt–PEt3
TIPS
3
NAME Sun-12032014-(TIPS,Pt)-C9-C8)2
EXPNO 1
PROCNO 1
Date_ 20140312
Time 20.37
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 40.3
DW 60.800 usec
DE 6.50 usec
TE 296.5 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1900153 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0 ppm
1.411
1.490
1.636
1.812
1.740
1.682
1.842
1.838
3.521
7.740
3.971
3.900
12.285
4.546
18.301
66.075
44.030
12.610
24.000


172.500
165.941
165.814
164.982
155.257
153.079
135.129
134.730
130.810
128.186
126.203
125.262
124.024
122.843
118.949
115.734
104.973
102.804
96.401
77.478
77.160
76.842
74.820
73.283
45.358
40.262
39.123
38.096
37.255
31.972
31.882
29.689
29.627
29.557
29.466
29.399
29.328
27.343
25.613
25.420
25.330
22.893
22.808
22.729
18.828
16.648
16.473
16.299
14.171
14.140
11.457
8.497
8.385
BRUKER
NAME Sun-12032014-(TIPS,Pt)-C9-C8)2
EXPNO 3
PROCNO 1
Date_ 20130906
Time 20.44
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1664
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 287
DW 20.800 usec
DE 6.50 usec
TE 297.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6278512 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
115.734
104.973
16.648
16.473
16.299
8.497
8.385
116 ppm
106 ppm
17 ppm
9 ppm
180
160
140
120
100
80
60
40
20
0 ppm

3

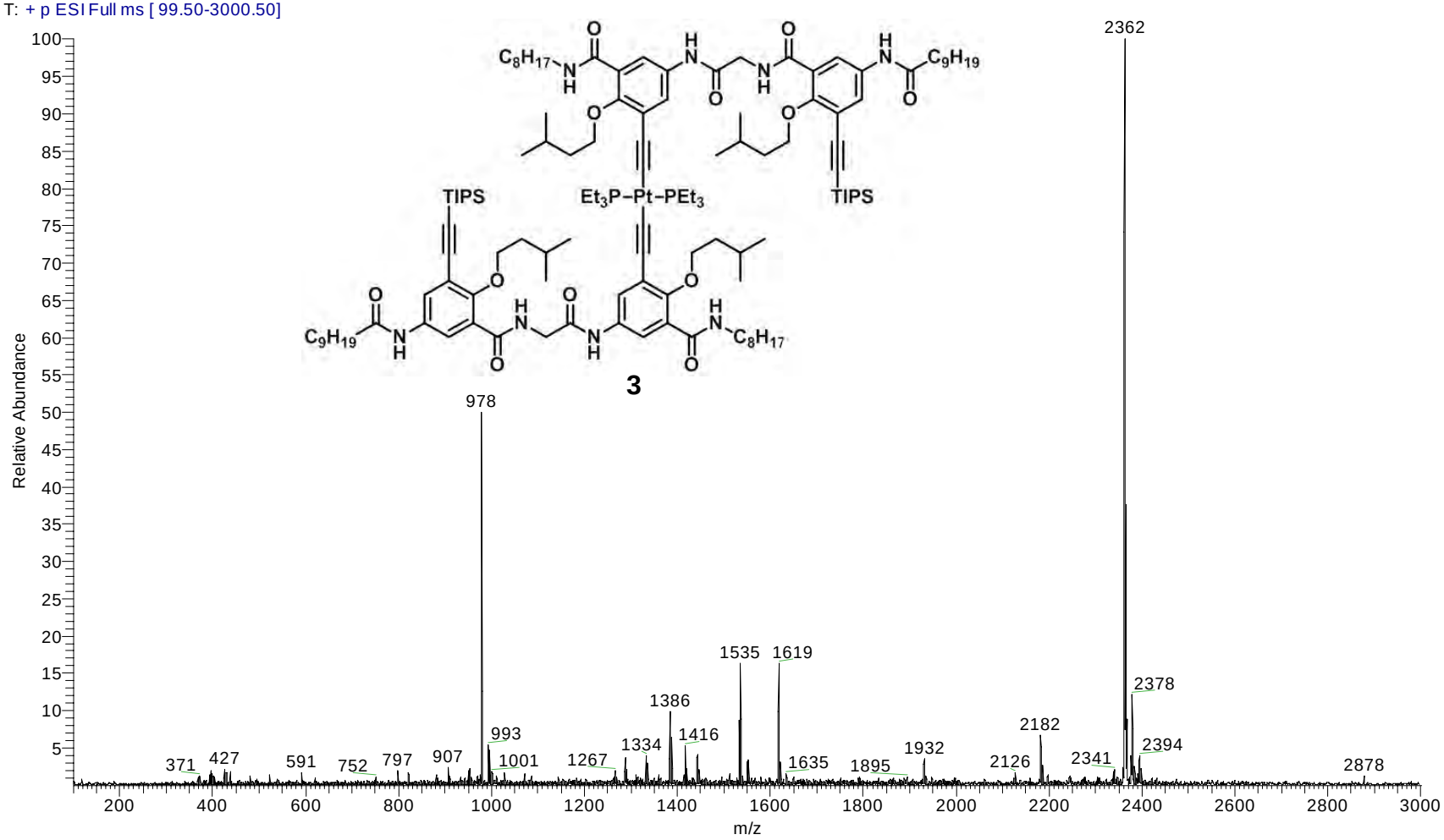


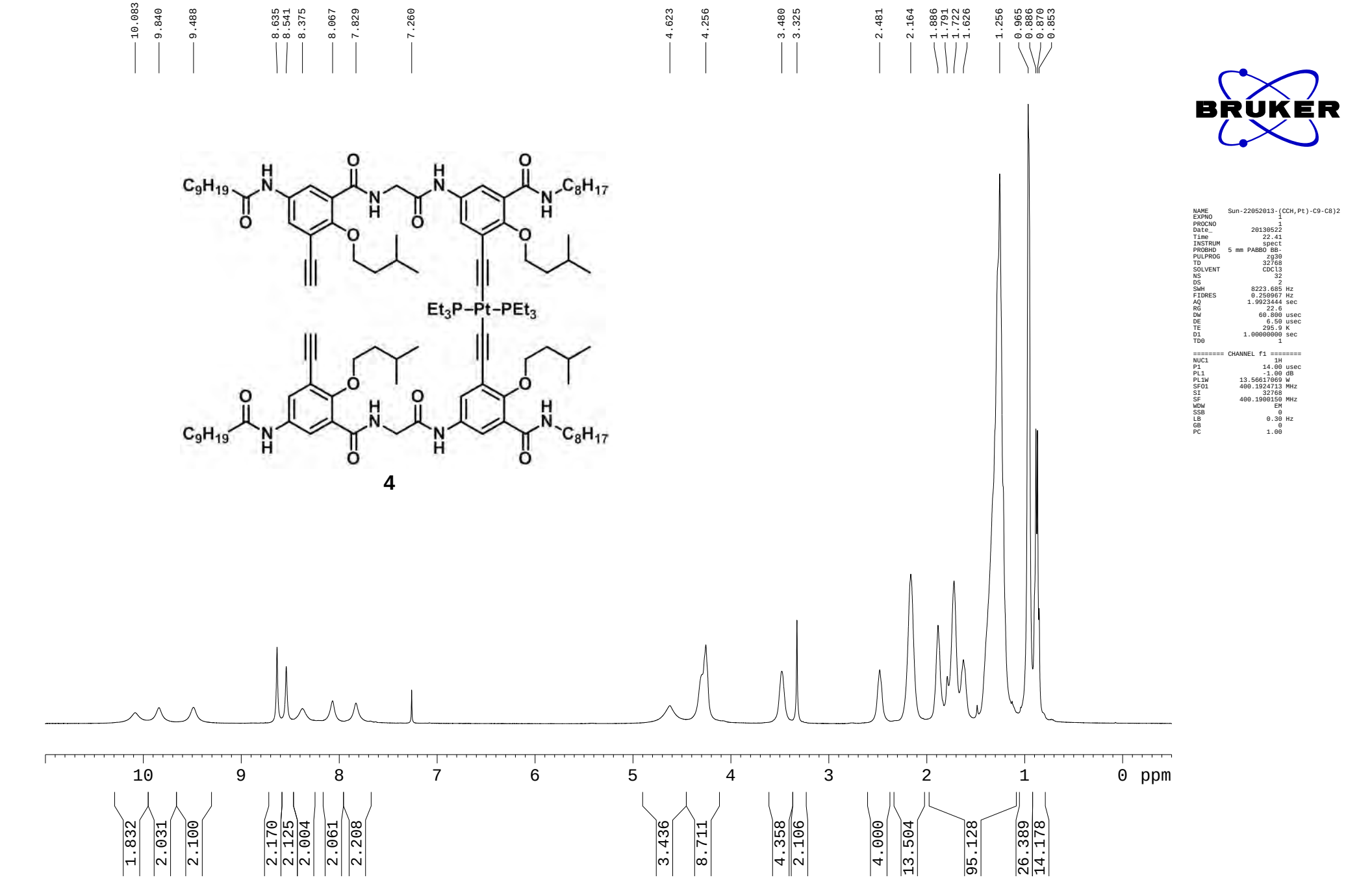
3

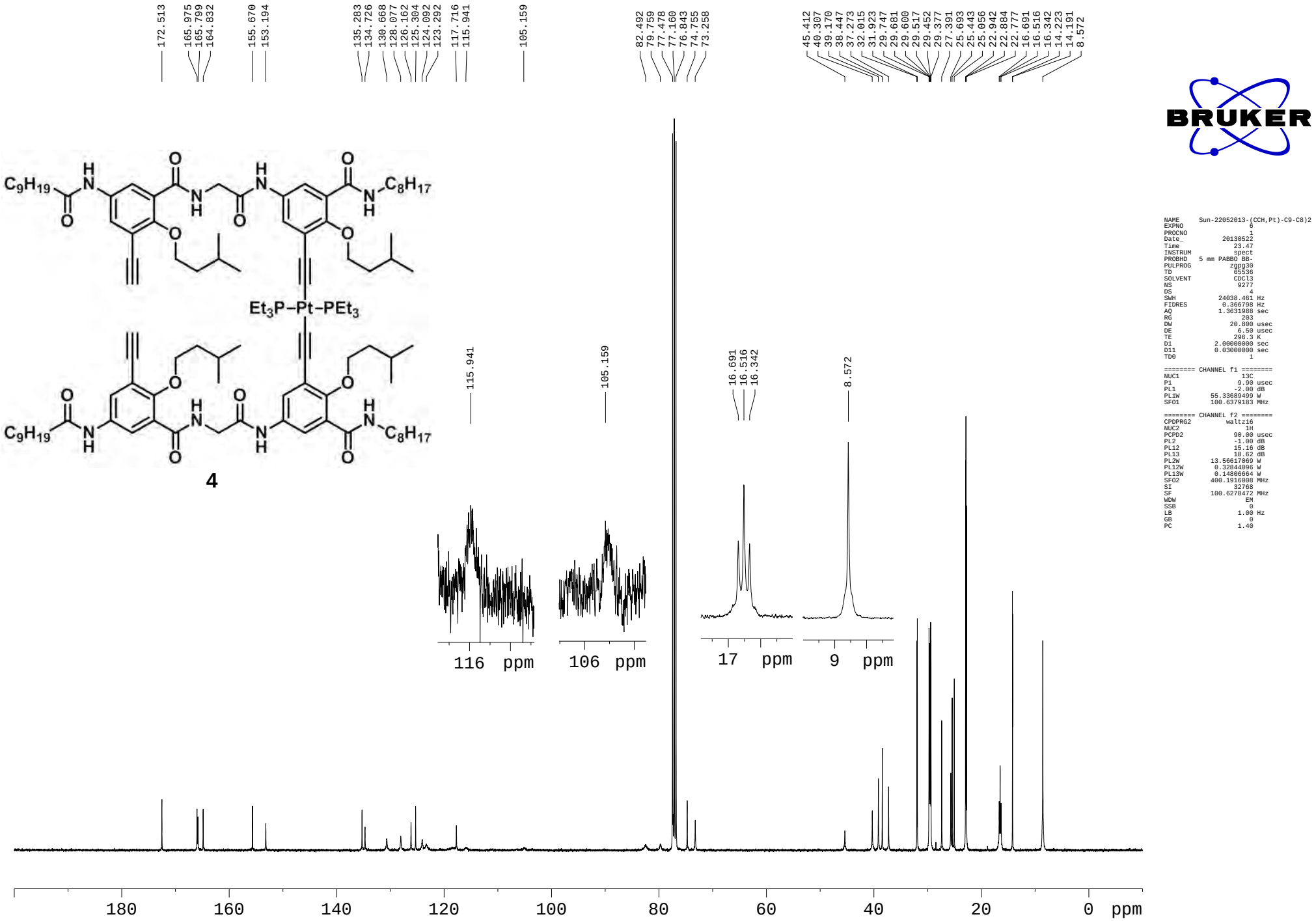

```
NAME          Sun-12032014-(TIPS,Pt)-C9-C8)2
EXPNO                  2
PROCNO                 1
Date_           20140701
Time                14.32
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG          zgdc30
TD                 65536
SOLVENT            CDCl3
NS                    70
DS                     4
SWH            64102.563 Hz
FIDRES         0.978127 Hz
AQ             0.5112308 sec
RG                  2050
DW                7.800 usec
DE                6.50 usec
TE                296.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  31P
P1                 14.70 usec
PL1                4.00 dB
PL1W         10.30000019 W
SFO1         161.9917814 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                  1H
PCPD2              90.00 usec
PL2                -1.00 dB
PL12               15.16 dB
PL2W         13.56617069 W
PL12W         0.32844096 W
SFO2         400.1916008 MHz
SI                 32768
SF           161.9998899 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

D:\MS_raw_data\hfc2063_140120154458 01/20/14 03:44:58 PM (TIPS,Pt)-C9-C8)2
ESI pos, 3kV, 15uL/min, w/ sheath gas, unknown conc.

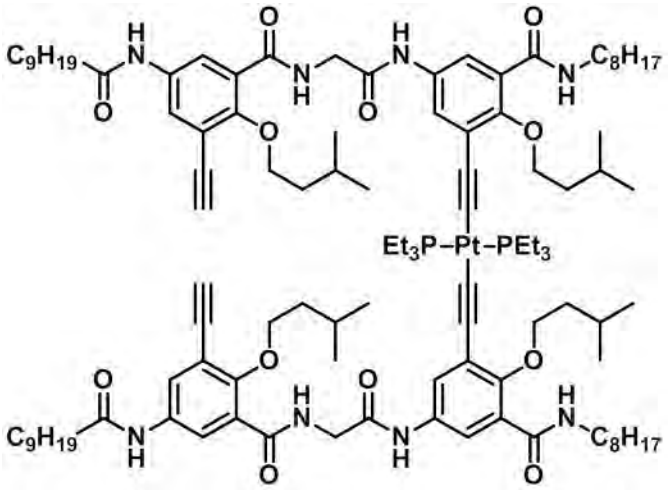
hfc2063_140120154458 #1-20 RT: 0.15-1.85 AV: 20 SM: 5G NL: 7.43E4
T: + p ESI Full ms [99.50-3000.50]




10.083
9.840
9.488
8.635
8.541
8.375
8.067
7.829
7.260
4.623
4.256
3.480
3.325
2.481
2.164
1.886
1.791
1.722
1.626
1.256
0.965
0.886
0.870
0.853
BRUKER
NAME Sun-22052013-(CCH,Pt)-C9-C8)2
EXPNO 1
PROCNO 1
Date_ 20130522
Time 22.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 22.6
DW 60.800 usec
DE 6.50 usec
TE 295.9 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1900150 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Et3P–Pt–PEt3
4
10
9
8
7
6
5
4
3
2
1
0 ppm
1.832
2.031
2.100
2.170
2.125
2.004
2.061
2.208
3.436
8.711
4.358
2.106
4.000
13.504
95.128
26.389
14.178




```
NAME        Sun-22052013-(CCH,Pt)-C9-C8)2
EXPNO                   6
PROCNO                  1
Date_             20130522
Time                23.47
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  9277
DS                     4
SWH            24038.461 Hz
FIDRES          0.366798 Hz
AQ              1.3631988 sec
RG                   203
DW                20.800 usec
DE                 6.50 usec
TE                296.3 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                  9.90 usec
PL1                -2.00 dB
PL1W         55.33689499 W
SFO1        100.6379183 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              90.00 usec
PL2                -1.00 dB
PL12               15.16 dB
PL13               18.62 dB
PL2W         13.56617069 W
PL12W         0.32844096 W
PL13W         0.14806664 W
SFO2        400.1916008 MHz
SI                 32768
SF          100.6278472 MHz
WDW                   EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

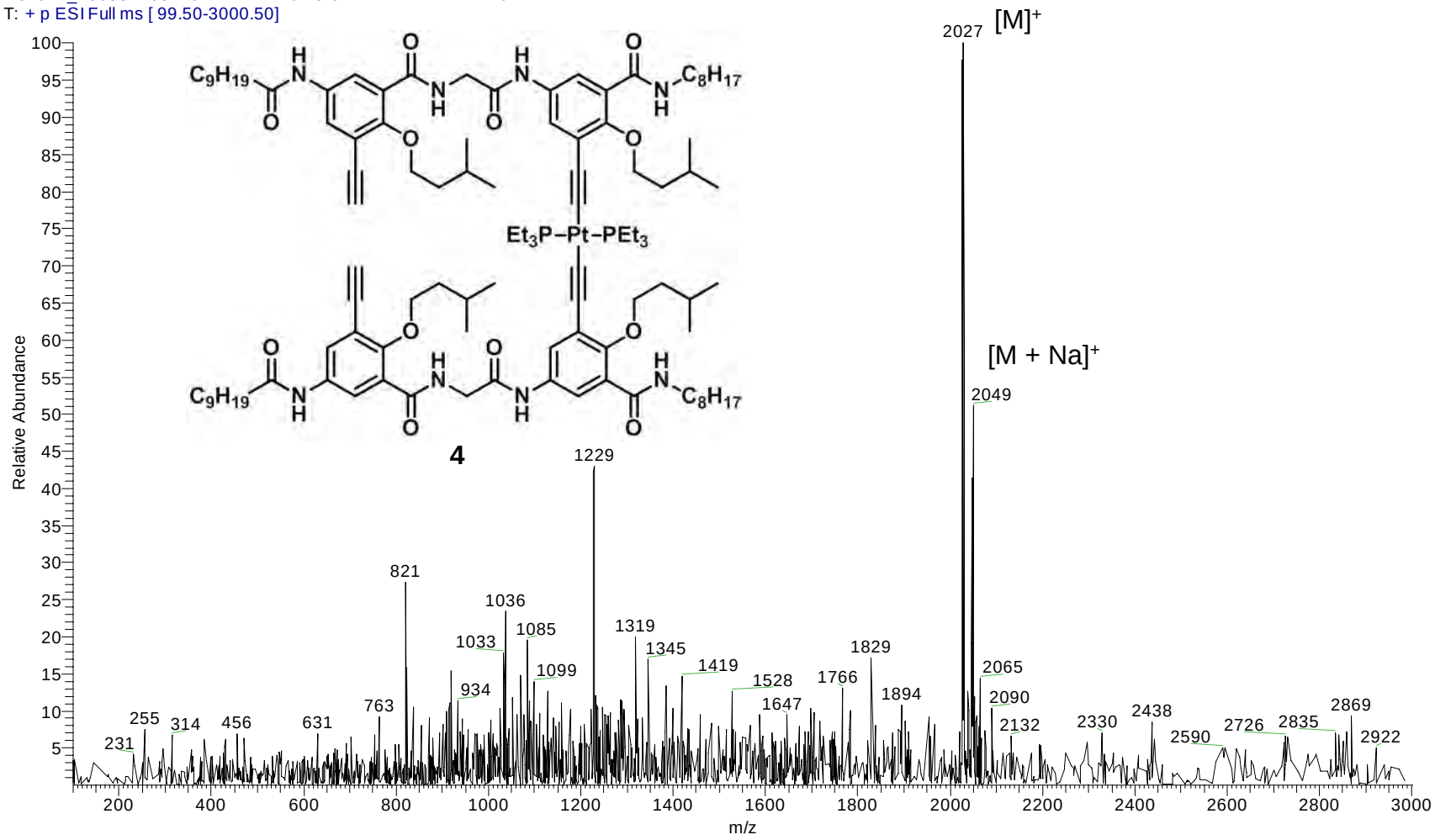


4

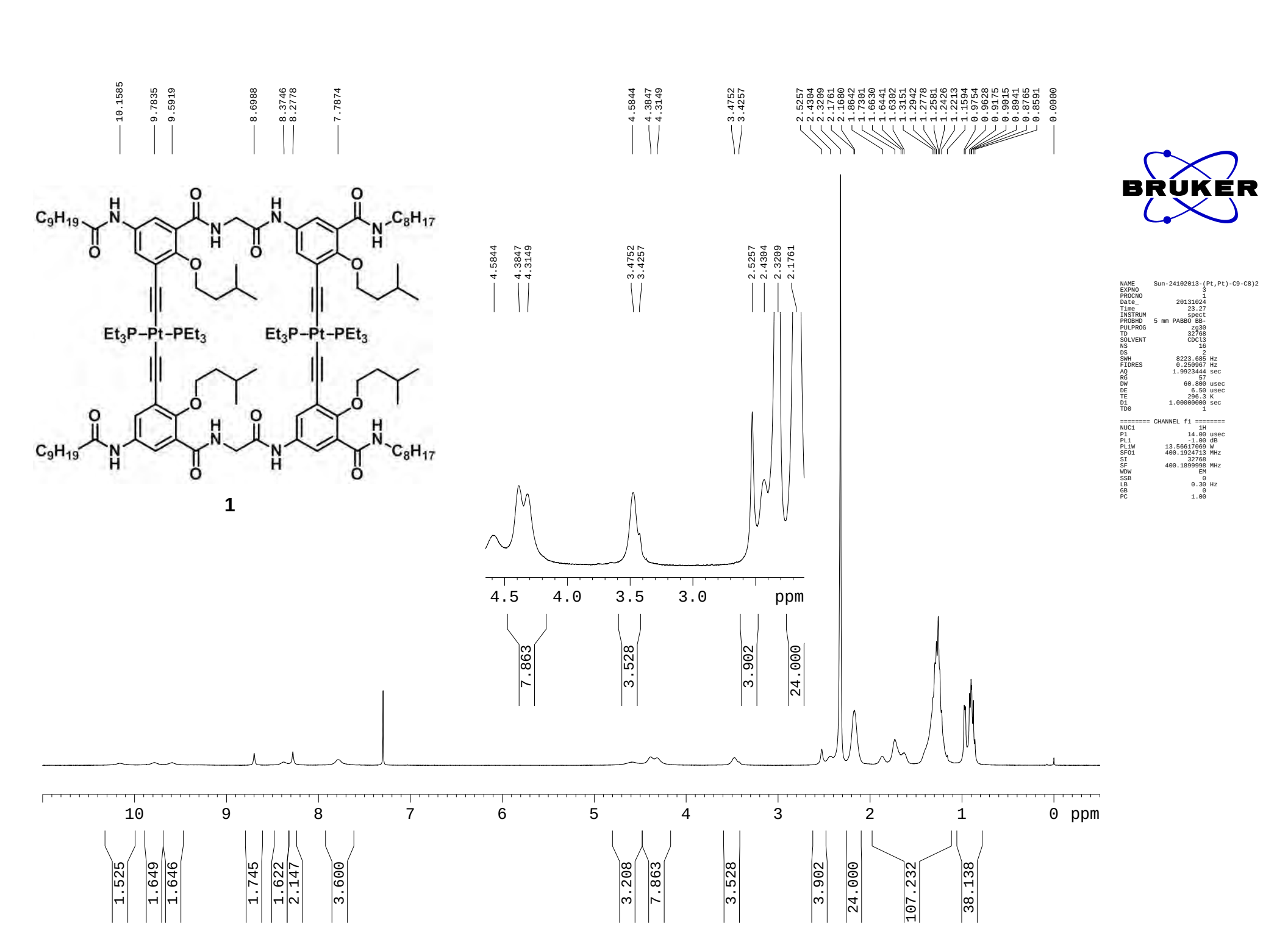

```
NAME        Sun-22052013-(CCH,Pt)-C9-C8)2
EXPNO                               2
PROCNO                              1
Date_                        20130522
Time                            22.46
INSTRUM                         spect
PROBHD     5 mm PABBO BB-
PULPROG                      zgdc30
TD                              65536
SOLVENT                         CDCl3
NS                                102
DS                                  4
SWH                       64102.563 Hz
FIDRES                     0.978127 Hz
AQ                        0.5112308 sec
RG                               2050
DW                              7.800 usec
DE                              6.50 usec
TE                              296.6 K
D1                       2.00000000 sec
D11                      0.03000000 sec
TD0                                 1

======== CHANNEL f1 ========
NUC1                              31P
P1                              14.70 usec
PL1                              4.00 dB
PL1W                    10.30000019 W
SFO1                   161.9917814 MHz

======== CHANNEL f2 ========
CPDPRG2                     waltz16
NUC2                              1H
PCPD2                           90.00 usec
PL2                             -1.00 dB
PL12                            15.16 dB
PL2W                    13.56617069 W
PL12W                    0.32844096 W
SFO2                   400.1916008 MHz
SI                             32768
SF                     161.9998899 MHz
WDW                               EM
SSB                                0
LB                              1.00 Hz
GB                                 0
PC                              1.40
```

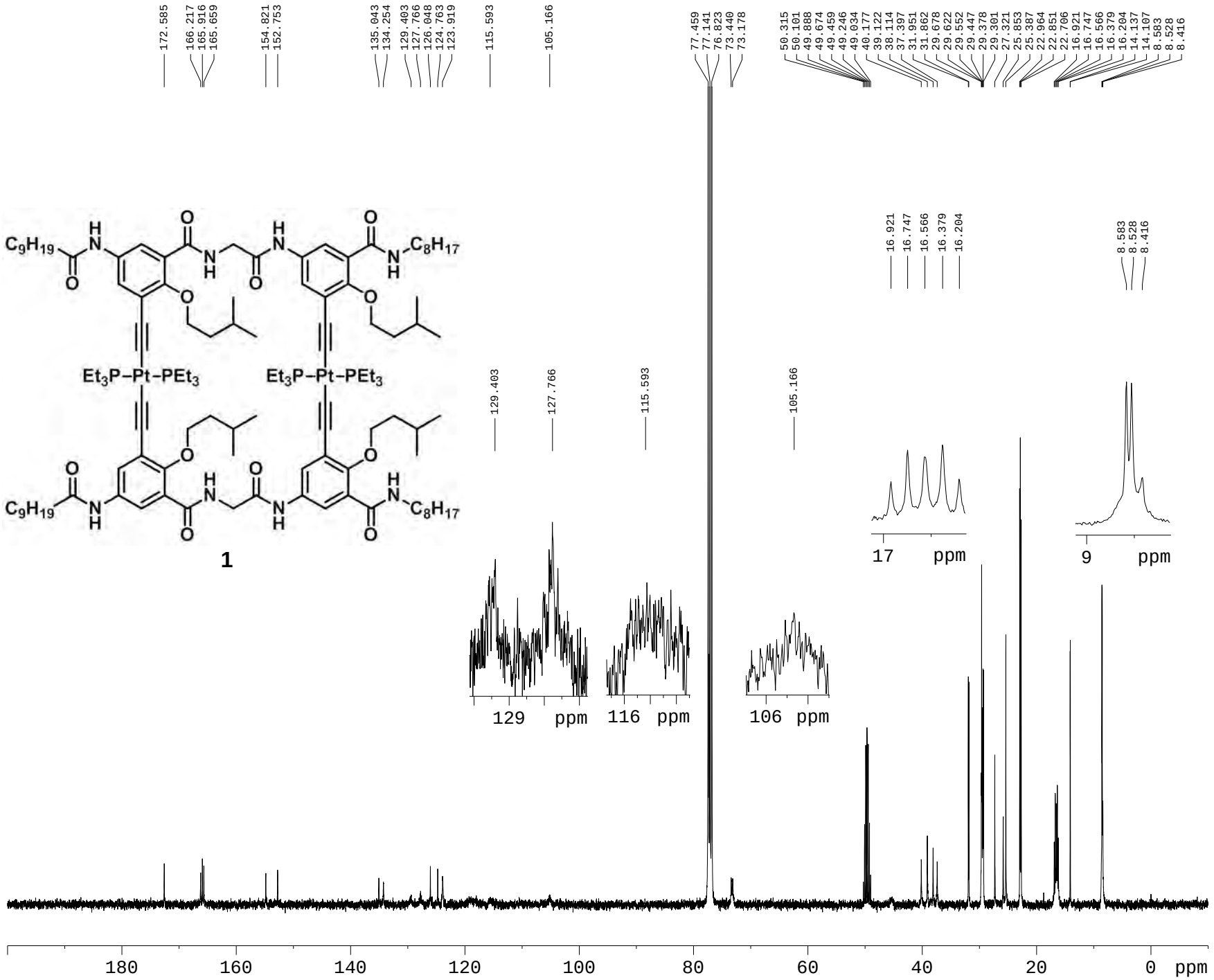
D:\MS_raw_data\hfc1614_130531165119 05/31/13 04:51:19 PM ((CCH, Pt)-C9-C8)2
ESI pos, 3kV, 3uL/min, w/o sheath gas, unknown conc.

hfc1614_130531165119 #1-2 RT: 0.15-0.24 AV: 2 NL: 2.10E4
T: + p ESI Full ms [99.50-3000.50]



4


10.1585
9.7835
9.5919
8.6988
8.3746
8.2778
7.7874
4.5844
4.3847
4.3149
3.4752
3.4257
2.5257
2.4304
2.3209
2.1761
2.1680
1.8642
1.7301
1.6630
1.6441
1.6302
1.3151
1.2942
1.2778
1.2581
1.2426
1.2213
1.1594
0.9754
0.9628
0.9175
0.9015
0.8941
0.8765
0.8591
0.0000
BRUKER
NAME Sun-24102013-(Pt,Pt)-C9-C8)2
EXPNO 3
PROCNO 1
Date_ 20131024
Time 23.27
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 57
DW 60.800 usec
DE 6.50 usec
TE 296.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1899998 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
Et3P–Pt–PEt3
Et3P–Pt–PEt3
1
4.5
4.0
3.5
3.0
ppm
7.863
3.528
3.902
24.000
10
9
8
7
6
5
4
3
2
1
0
ppm
1.525
1.649
1.646
1.745
1.622
2.147
3.600
3.208
7.863
3.528
3.902
24.000
107.232
38.138



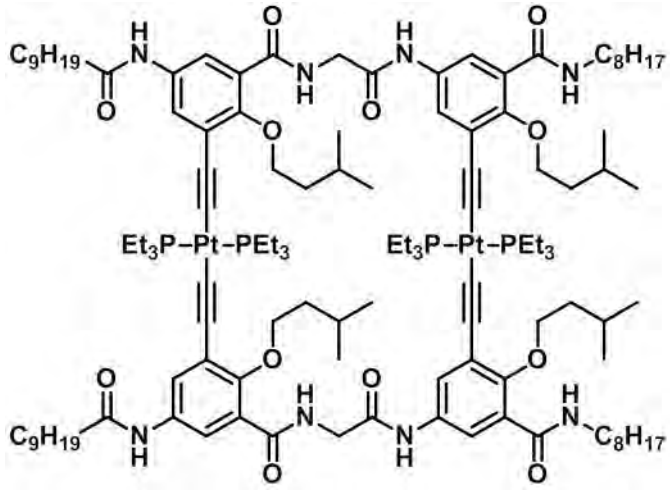
Current Data Parameters
NAME Sun-24102013-(Pt,Pt)-C9-C8)2
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20131025
Time 9.15
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 10138
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 296.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1

======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33680499 W
SFO1 100.6379183 MHz

======== CHANNEL f2 ========
CPDPRG[2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz

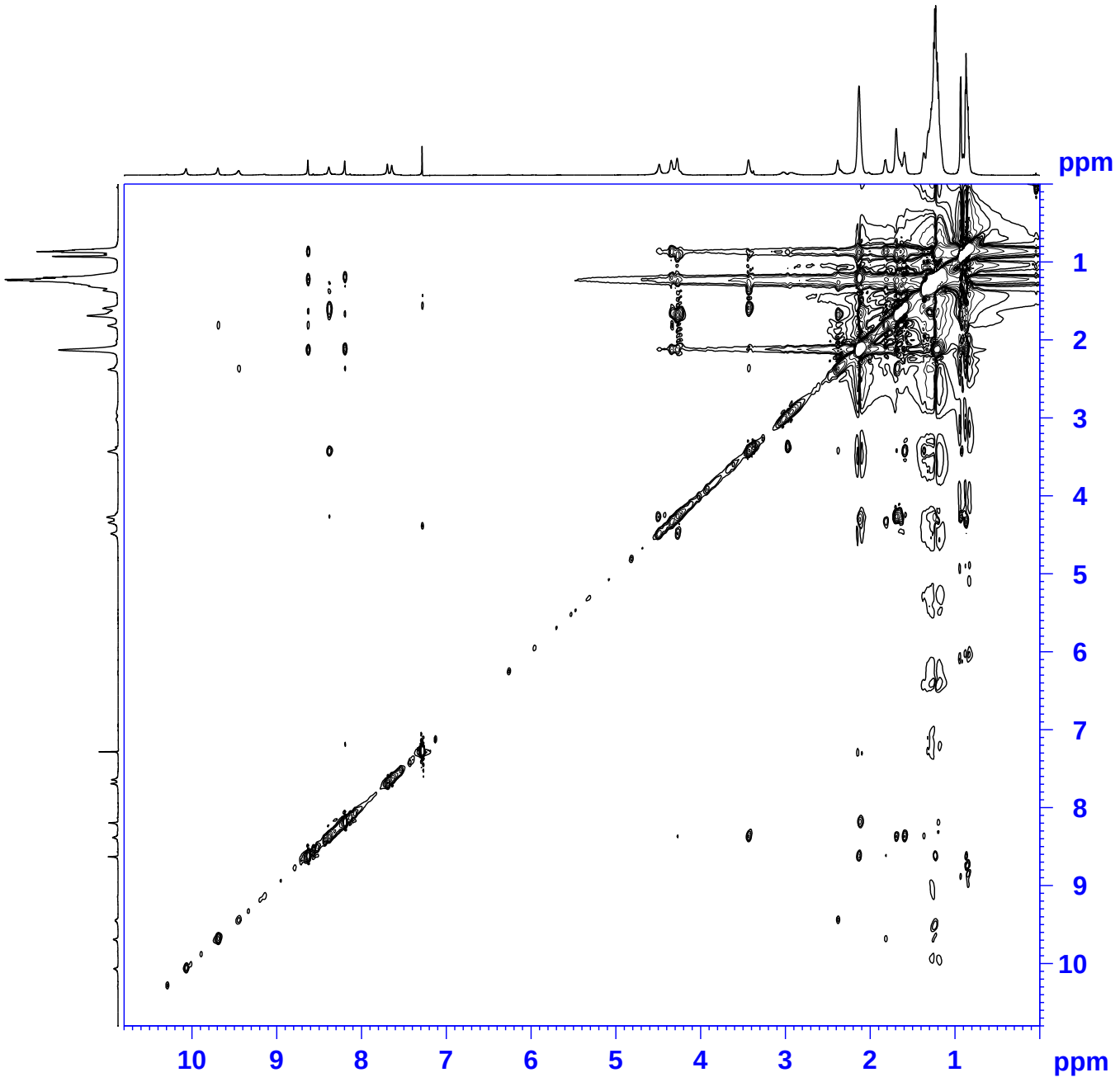
F2 - Processing parameters
SI 32768
SF 100.6278493 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



1


```
NAME      Sun-24102013-(Pt,Pt)-C9-C8)2
EXPNO                4
PROCNO               1
Date_         20131024
Time              23.30
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG         zgdc30
TD               65536
SOLVENT          CDCl3
NS                 512
DS                   4
SWH           64102.563 Hz
FIDRES         0.978127 Hz
AQ             0.5112308 sec
RG                2050
DW                7.800 usec
DE                6.50 usec
TE               296.8 K
D1            2.00000000 sec
D11           0.03000000 sec
TD0                  1

======== CHANNEL f1 ========
NUC1               31P
P1                14.70 usec
PL1                4.00 dB
PL1W        10.30000019 W
SFO1       161.9917814 MHz

======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2               1H
PCPD2             90.00 usec
PL2               -1.00 dB
PL12              15.16 dB
PL2W        13.56617069 W
PL12W        0.32844096 W
SFO2       400.1916008 MHz
SI                32768
SF         161.9998899 MHz
WDW                EM
SSB                0
LB              1.00 Hz
GB                 0
PC              1.40
```

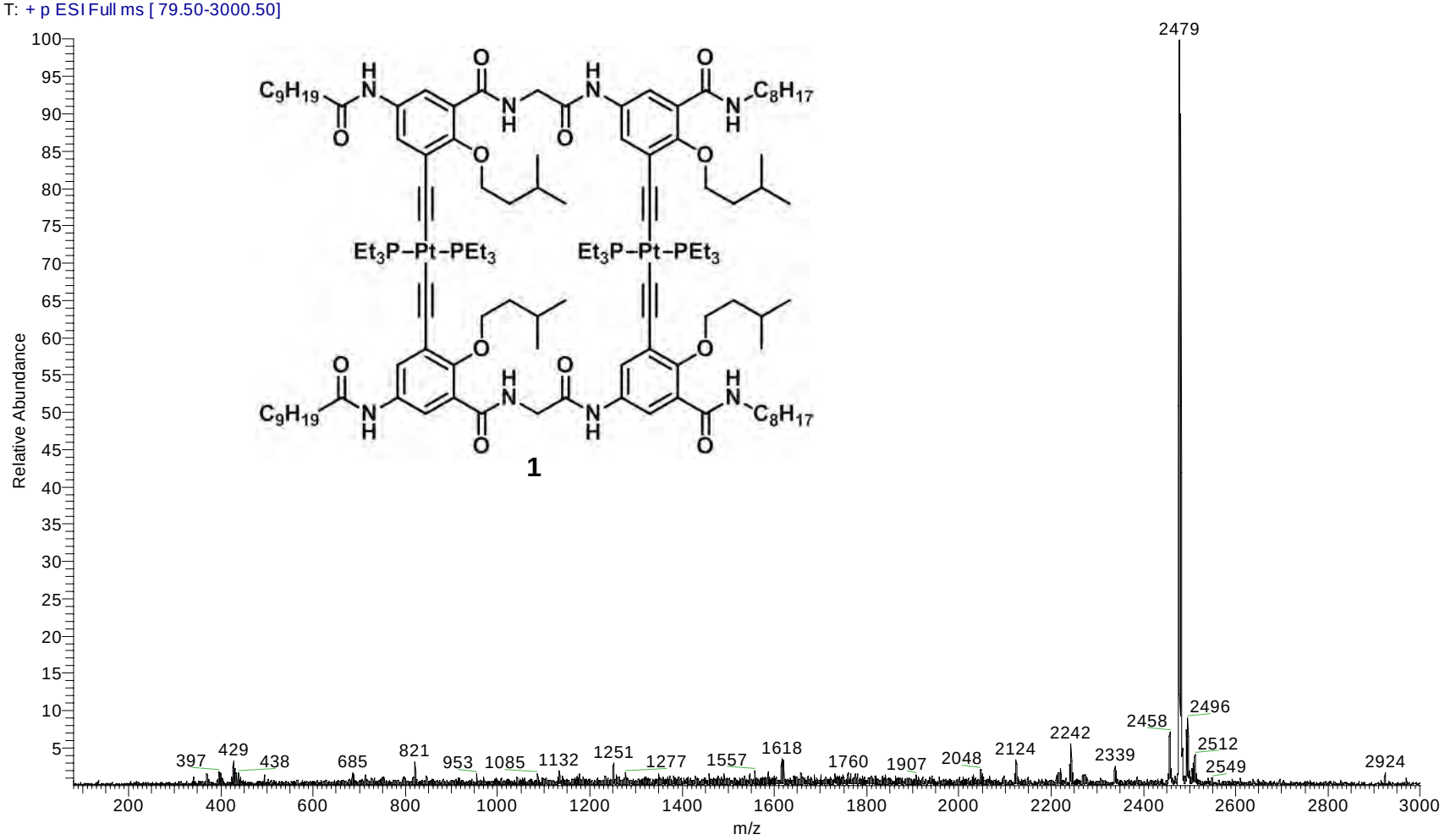
ROESY spectrum of **1** in 2% $CD_3OH/CDCl_3$ at 7 mM with water supression



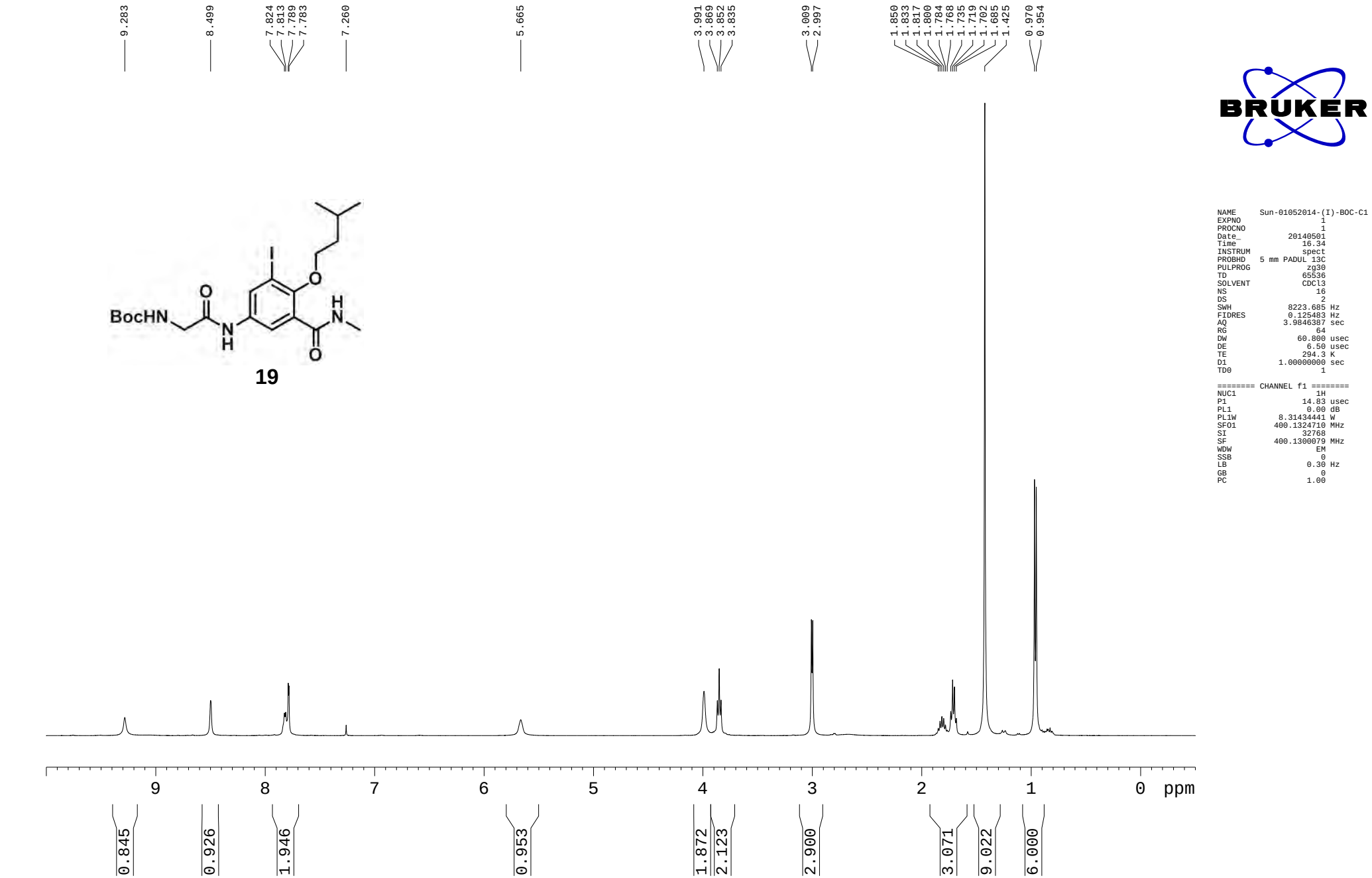

```
NAME          Sun-27082013-Pt2-CD MeOH 700
EXPNO                   15
PROCNO                   1
Date_             20130828
Time                  5.24
INSTRUM              spect
PROBHD    5 mm CPTCI 1H-
PULPROG          roesyphpr
TD                    2048
SOLVENT              CDCl3
NS                      16
DS                      16
SWH              14097.744 Hz
FIDRES            6.883664 Hz
AQ               0.0726857 sec
RG                      64
DW                  35.467 usec
DE                  10.00 usec
TE                  298.0 K
D0               0.00002638 sec
D1               2.00000000 sec
D11              0.03000000 sec
D12              0.00002000 sec
D13              0.00000400 sec
IN0              0.00007100 sec

======== CHANNEL f1 ========
SFO1            700.2120824 MHz
NUC1                    1H
P1                   8.04 usec
P15               200000.00 usec
ND0                     1
TD                    256
SFO1             700.2121 MHz
FIDRES          55.017605 Hz
SW                 20.115 ppm
FnMODE         States-TPPI
SI                    2048
SF              700.2100000 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
PC                   1.00
SI                    1024
MC2            States-TPPI
SF              700.2100000 MHz
WDW                 QSINE
SSB                     2
LB                   0.00 Hz
GB                      0
```

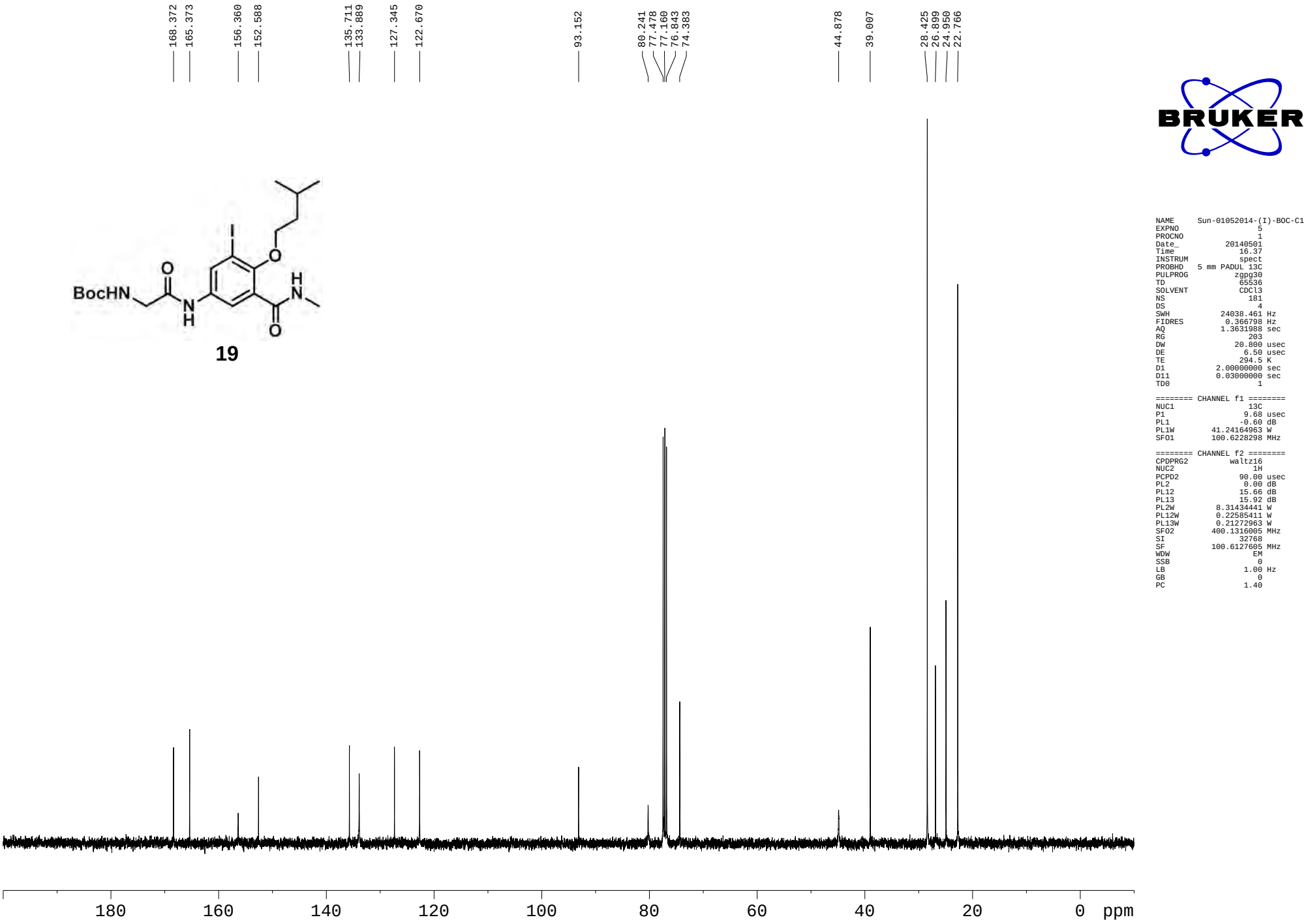
D:\MS_raw_data\hfc2000_130916163036 09/16/13 04:30:36 PM Pt2-CD-1
ESI pos, 3kV, 15uL/min, w/ sheath gas, unknown conc

hfc2000_130916163036 #1-39 RT: 0.13-3.25 AV: 39 SM: 5G NL: 2.85E4
T: + p ESI Full ms [79.50-3000.50]



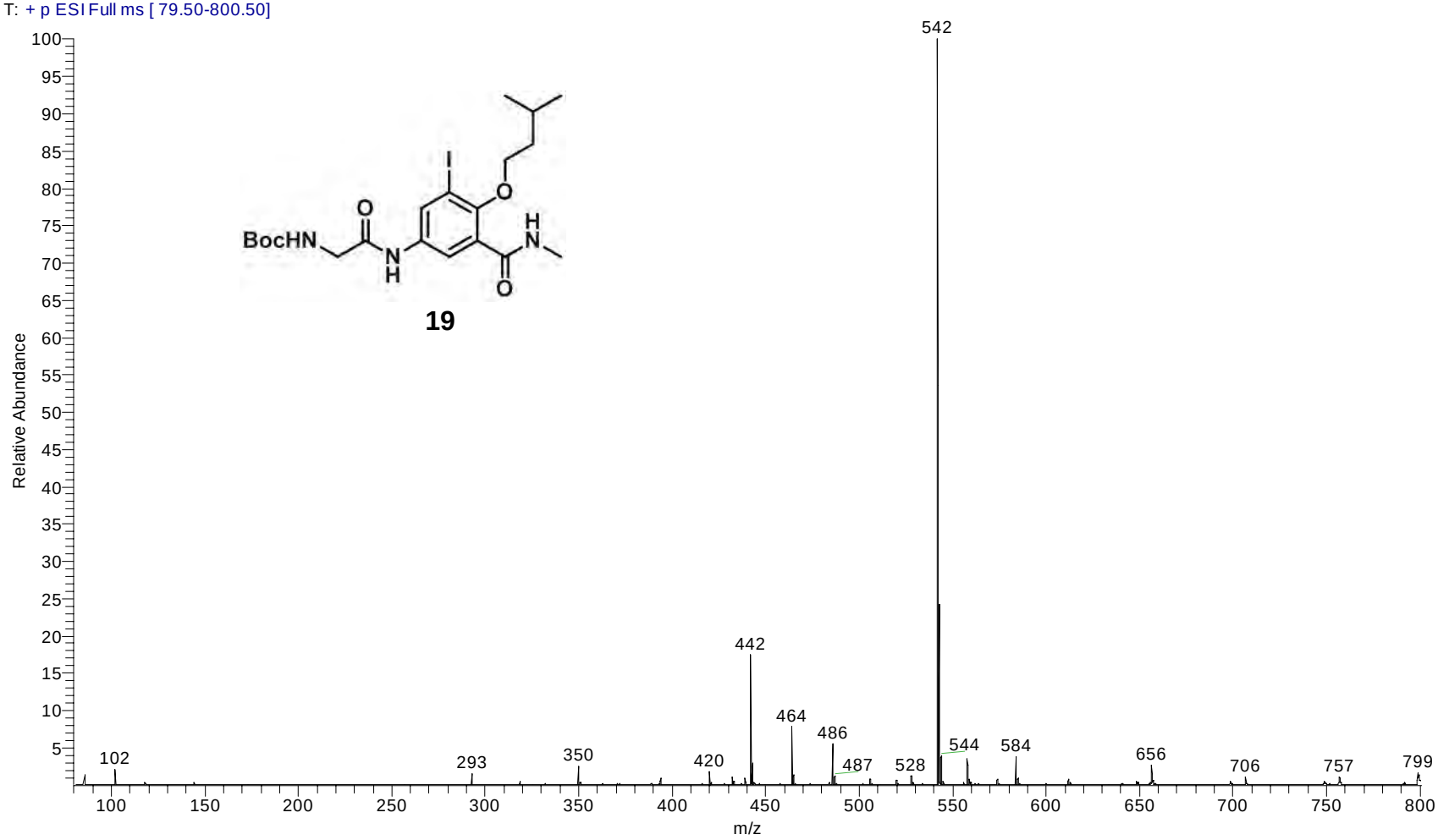
1


9.283
8.499
7.824
7.813
7.789
7.783
7.260
5.665
3.991
3.869
3.852
3.835
3.009
2.997
1.850
1.833
1.817
1.800
1.784
1.768
1.735
1.719
1.702
1.685
1.425
0.970
0.954
BocHN
O
N
H
I
O
H
N
O
19
NAME Sun-01052014-(I)-BOC-C1
EXPNO 1
PROCNO 1
Date_ 20140501
Time 16.34
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 64
DW 60.800 usec
DE 6.50 usec
TE 294.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.83 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300079 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
0.845
0.926
1.946
0.953
1.872
2.123
2.900
3.071
9.022
6.000

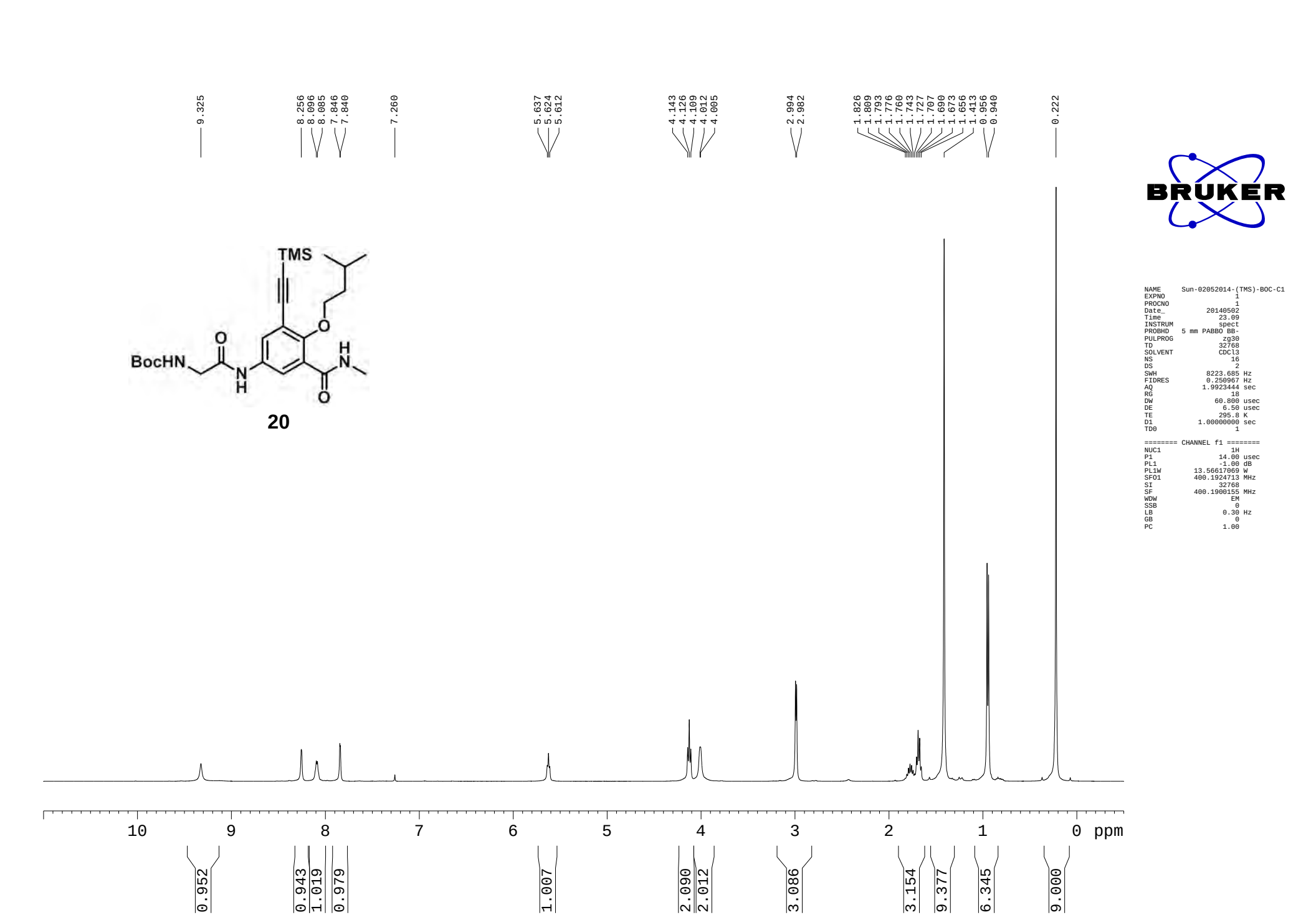

168.372
165.373
156.360
152.588
135.711
133.889
127.345
122.670
93.152
80.241
77.478
77.160
76.843
74.383
44.878
39.007
28.425
26.899
24.950
22.766
BocHN
I
O
N
H
H
N
O
O
19
NAME Sun-01052014-(I)-BOC-C1
EXPNO 5
PROCNO 1
Date_ 20140501
Time 16.37
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 181
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 294.5 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.68 usec
PL1 -0.60 dB
PL1W 41.24164963 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 15.66 dB
PL13 15.92 dB
PL2W 8.31434441 W
PL12W 0.22585411 W
PL13W 0.21272963 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127605 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

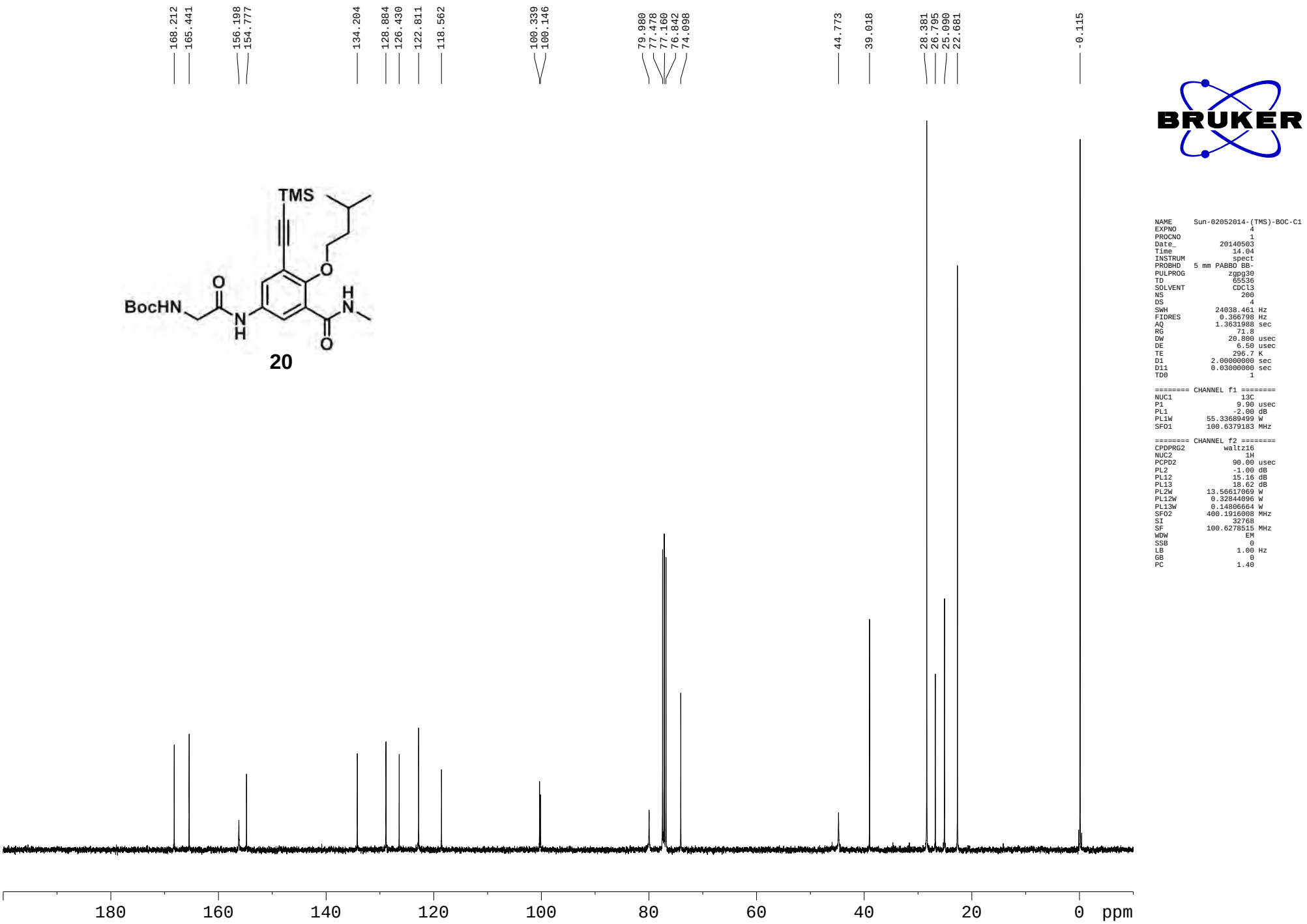
D:\MS_raw_data\hfc1994 08/28/13 02:56:22 PM (TIPS,ic5)-C1-CO2Me
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

hfc1994 #2-4 RT: 0.21-0.37 AV: 3 SM: 5G NL: 3.73E6
T: + p ESI Full ms [79.50-800.50]



19


9.325
8.256
8.096
8.085
7.846
7.840
7.260
5.637
5.624
5.612
4.143
4.126
4.109
4.012
4.005
2.994
2.982
1.826
1.809
1.793
1.776
1.760
1.743
1.727
1.707
1.690
1.673
1.656
1.413
0.956
0.940
0.222
TMS
BocHN
O
N
H
O
H
N
O
20
BRUKER
NAME Sun-02052014-(TMS)-BOC-C1
EXPNO 1
PROCNO 1
Date_ 20140502
Time 23.09
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 18
DW 60.800 usec
DE 6.50 usec
TE 295.8 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1900155 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0
ppm
0.952
0.943
1.019
0.979
1.007
2.090
2.012
3.086
3.154
9.377
6.345
9.000

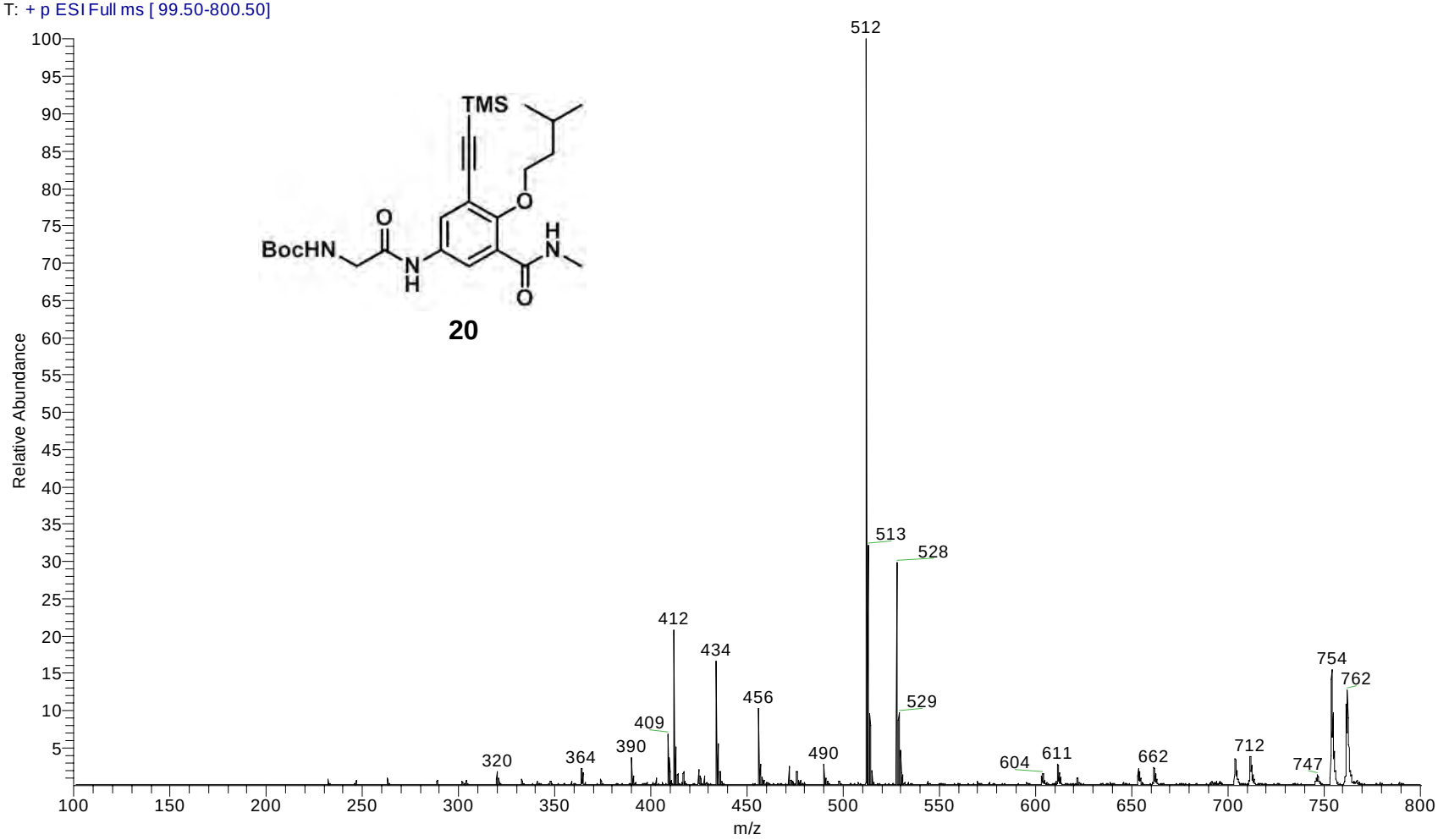


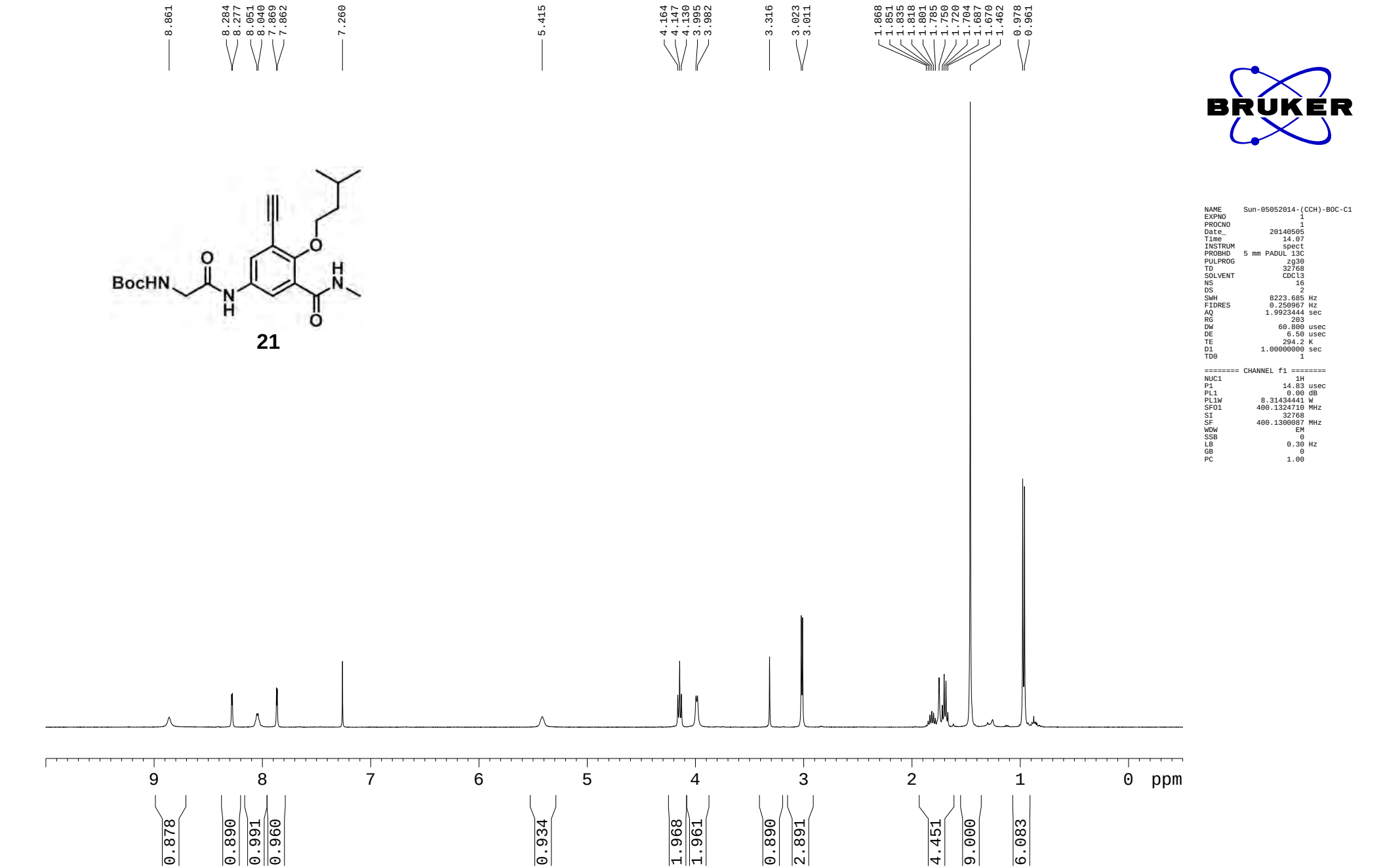
BRUKER

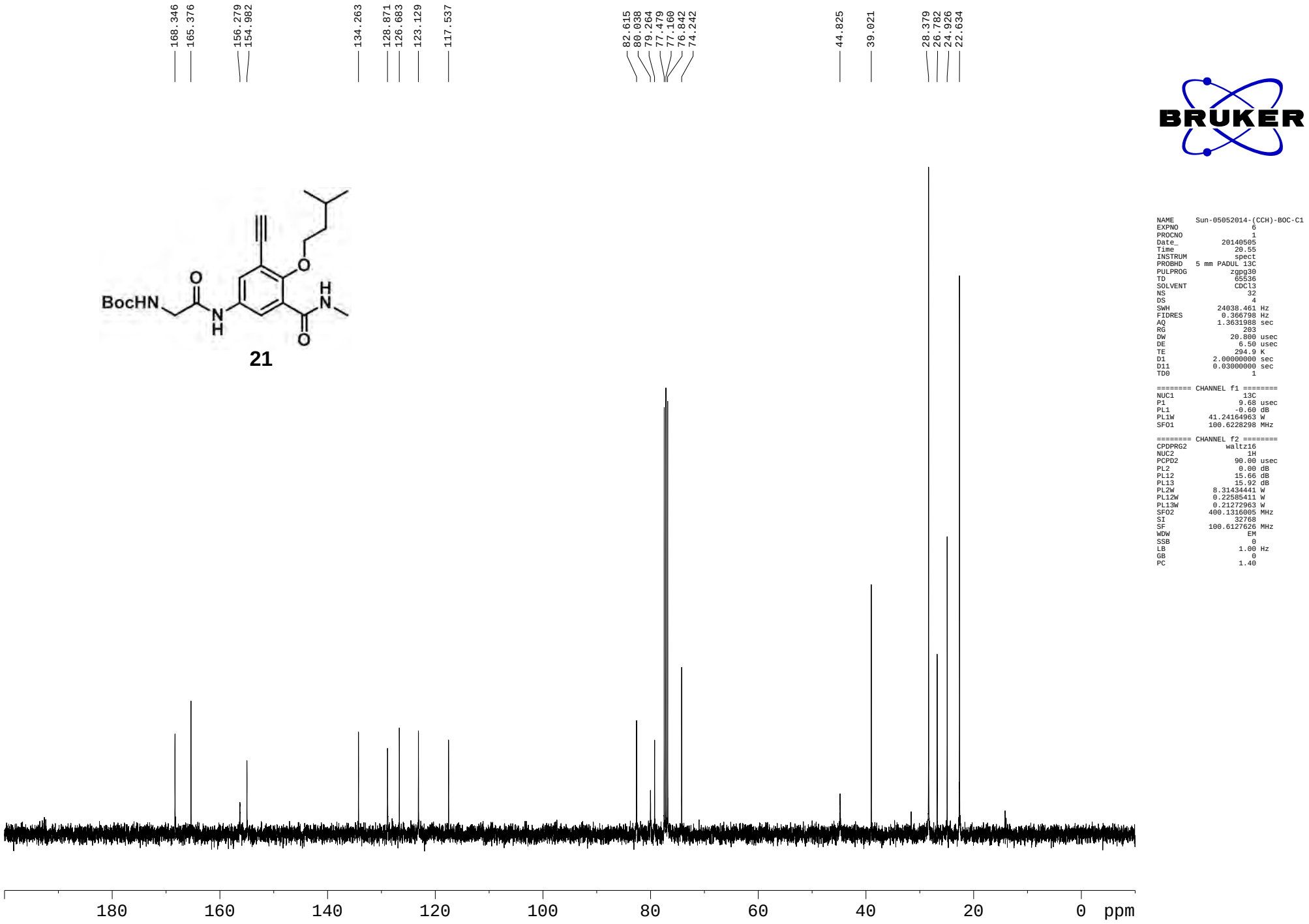
```
NAME          Sun-02052014-(TMS)-BOC-C1
EXPNO                    4
PROCNO                   1
Date_             20140503
Time                 14.04
INSTRUM              spect
PROBHD     5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                   200
DS                     4
SWH              24038.461 Hz
FIDRES           0.366798 Hz
AQ               1.3631988 sec
RG                   71.8
DW                  20.800 usec
DE                   6.50 usec
TE                  296.7 K
D1               2.00000000 sec
D11              0.03000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   13C
P1                    9.90 usec
PL1                  -2.00 dB
PL1W           55.33689499 W
SFO1          100.6379183 MHz

======== CHANNEL f2 ========
CPDPRG2            waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 15.16 dB
PL13                 18.62 dB
PL2W           13.56617069 W
PL12W           0.32844096 W
PL13W           0.14806664 W
SFO2          400.1916008 MHz
SI                   32768
SF            100.6278515 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.40
```

D:\MS_raw_data\hfc2114_140613170333 06/13/14 05:03:33 PM (TMS,ic5)-Boc-C1
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc

hfc2114_140613170333 #1-2 RT: 0.13-0.21 AV: 2 SM: 5G NL: 1.05E6
T: + p ESI Full ms [99.50-800.50]

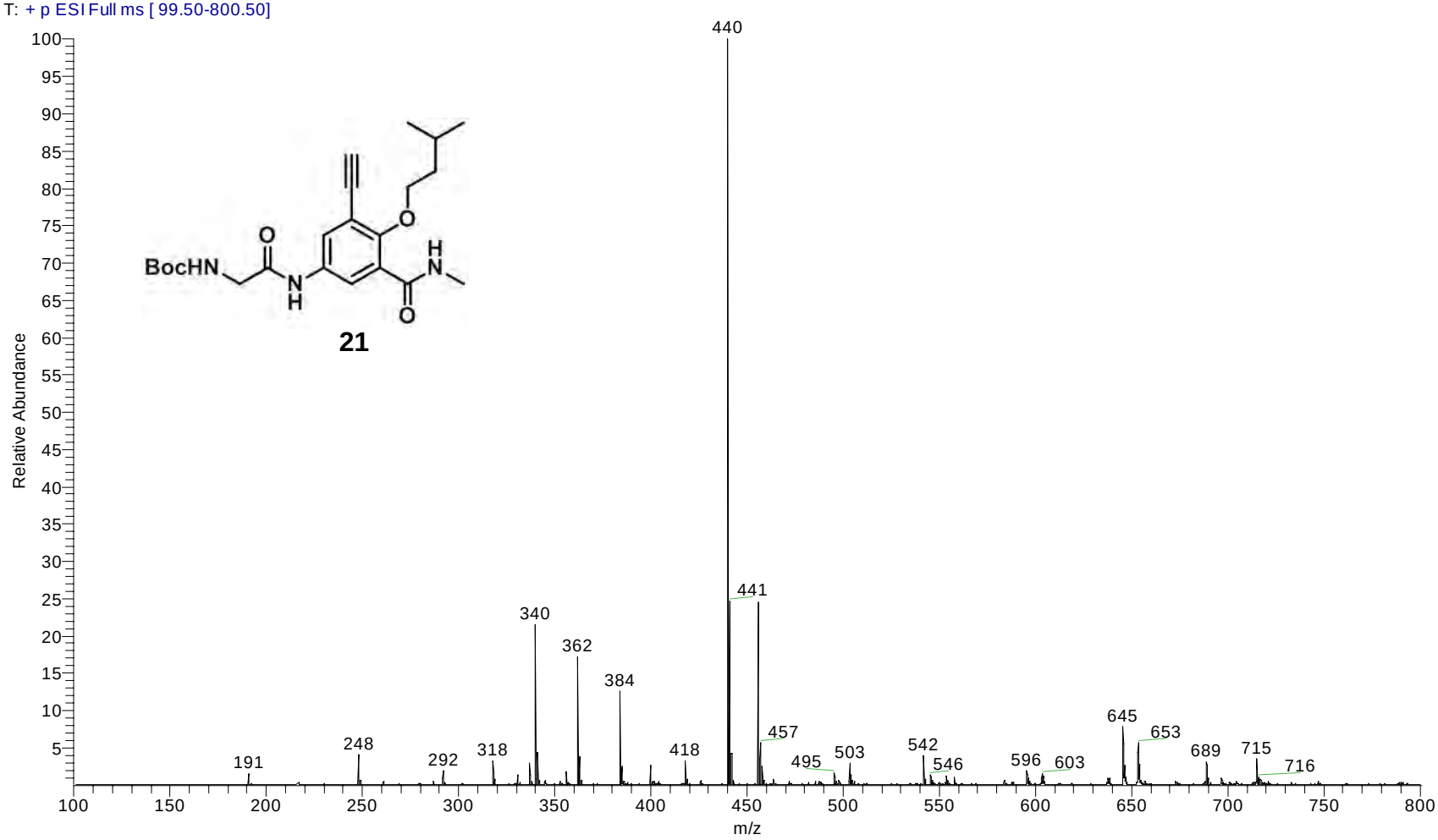


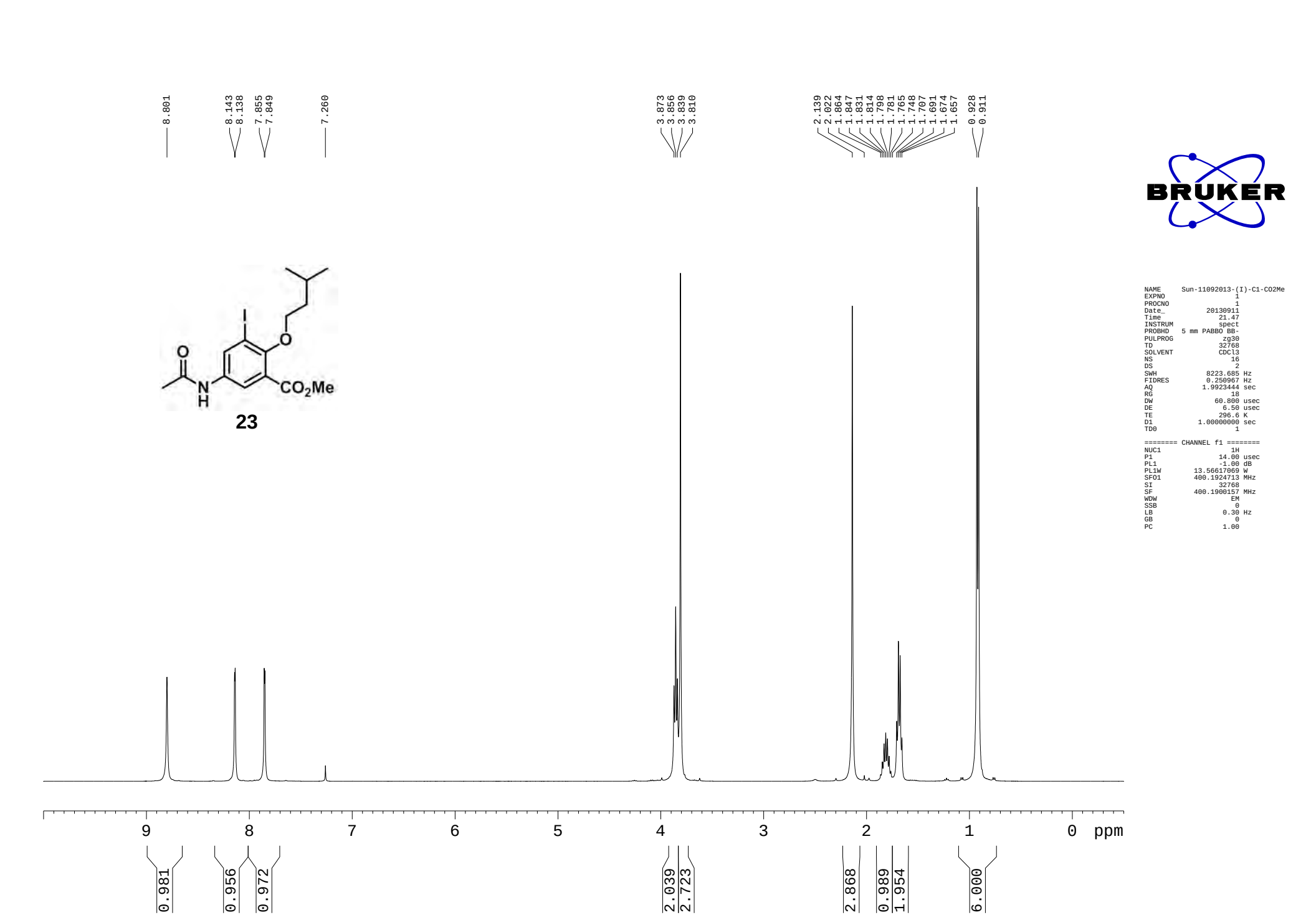

8.861
8.284
8.277
8.051
8.040
7.869
7.862
7.260
5.415
4.164
4.147
4.130
3.995
3.982
3.316
3.023
3.011
1.868
1.851
1.835
1.818
1.801
1.785
1.750
1.720
1.704
1.687
1.670
1.462
0.978
0.961
BocHN
O
N
H
O
O
H
N
21
NAME Sun-05052014-(CCH)-BOC-C1
EXPNO 1
PROCNO 1
Date_ 20140505
Time 14.07
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 203
DW 60.800 usec
DE 6.50 usec
TE 294.2 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.83 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1300087 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
0.878
0.890
0.991
0.960
0.934
1.968
1.961
0.890
2.891
4.451
9.000
6.083

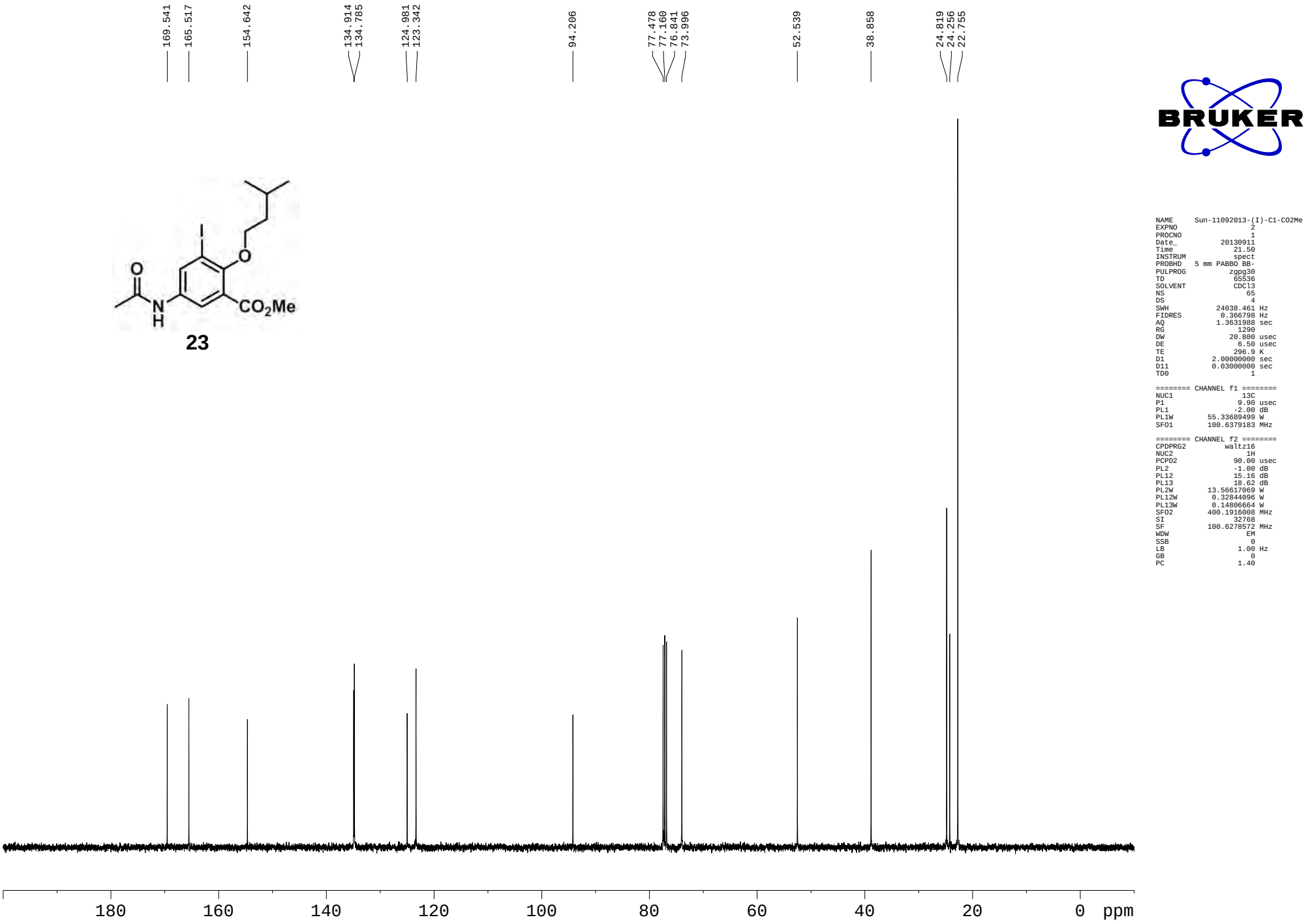

168.346
165.376
156.279
154.982
134.263
128.871
126.683
123.129
117.537
82.615
80.038
79.264
77.479
77.160
76.842
74.242
44.825
39.021
28.379
26.782
24.926
22.634
BocHN
O
N
H
O
O
H
N
21
NAME Sun-05052014-(CCH)-BOC-C1
EXPNO 6
PROCNO 1
Date_ 20140505
Time 20.55
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 32
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 203
DW 20.800 usec
DE 6.50 usec
TE 294.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.68 usec
PL1 -0.60 dB
PL1W 41.24164963 W
SFO1 100.6228298 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 0.00 dB
PL12 15.66 dB
PL13 15.92 dB
PL2W 8.31434441 W
PL12W 0.22585411 W
PL13W 0.21272963 W
SFO2 400.1316005 MHz
SI 32768
SF 100.6127626 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

D:\MS_raw_data\hfc1996 09/09/13 11:29:24 AM (CCH,ic5)-BOC-C1
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

hfc1996 #1-3 RT: 0.13-0.29 AV: 3 SM: 5G NL: 1.35E6
T: + p ESI Full ms [99.50-800.50]

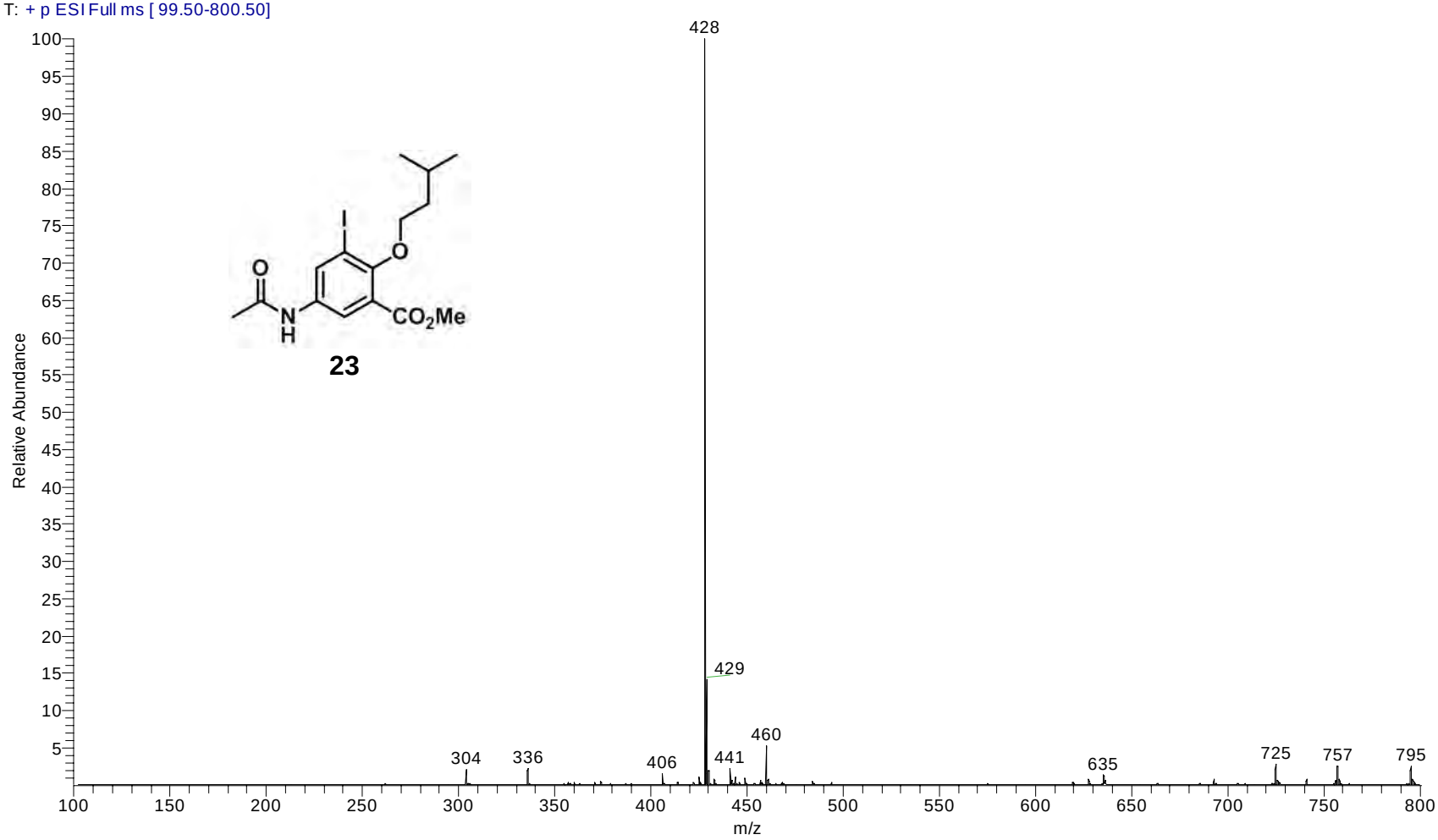



8.801
8.143
8.138
7.855
7.849
7.260
3.873
3.856
3.839
3.810
2.139
2.022
2.004
1.847
1.831
1.814
1.798
1.781
1.765
1.748
1.707
1.691
1.674
1.657
0.928
0.911
BRUKER
NAME Sun-11092013-(I)-C1-CO2Me
EXPNO 1
PROCNO 1
Date_ 20130911
Time 21.47
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 18
DW 60.800 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1900157 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
I
O
O
N
H
CO2Me
23
9
8
7
6
5
4
3
2
1
0
ppm
0.981
0.956
0.972
2.039
2.723
2.868
0.989
1.954
6.000

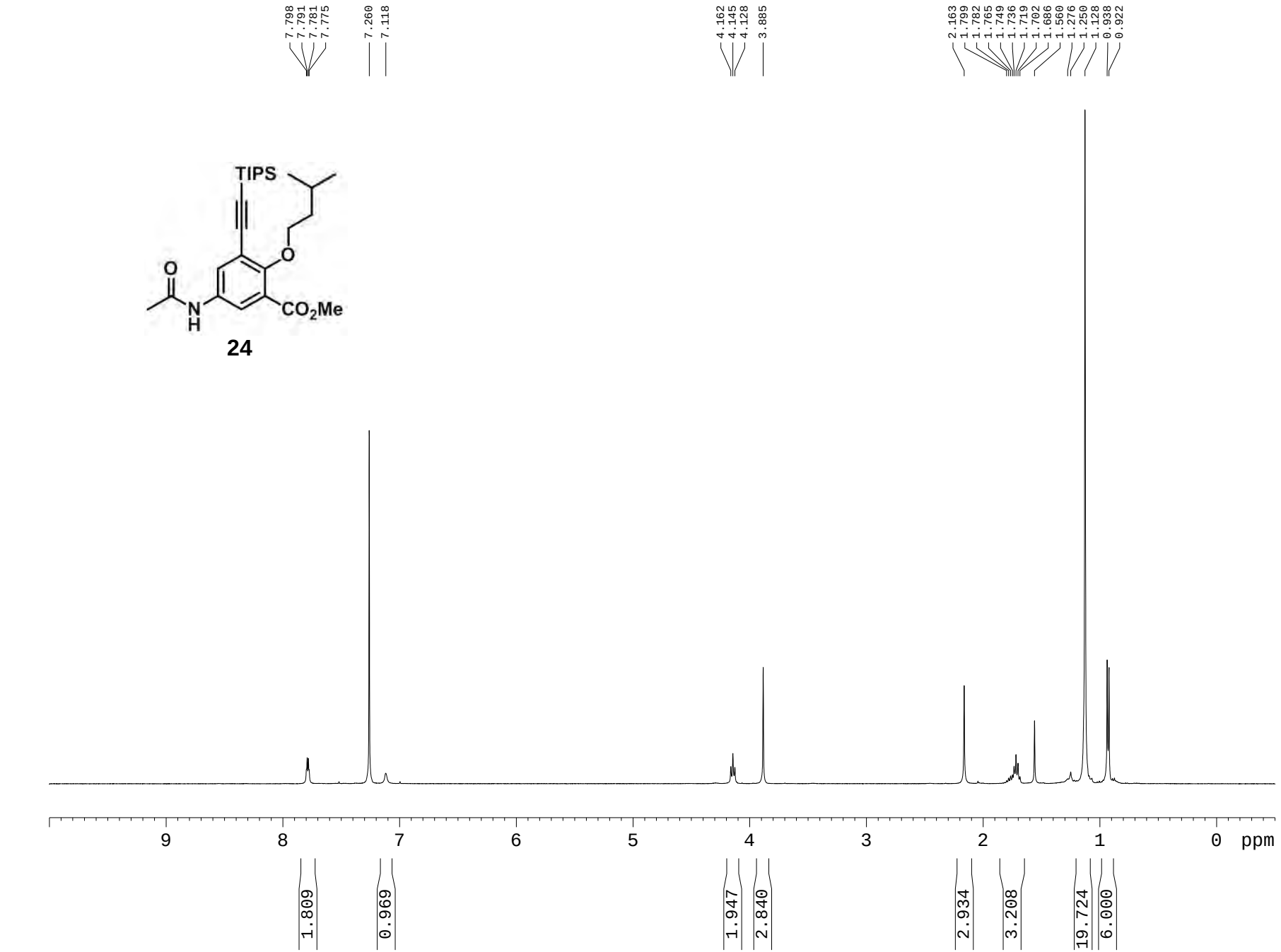

169.541
165.517
154.642
134.914
134.785
124.981
123.342
94.206
77.478
77.160
76.841
73.996
52.539
38.858
24.819
24.256
22.755
O
I
O
N
H
CO2Me
23
NAME Sun-11092013-(I)-C1-CO2Me
EXPNO 2
PROCNO 1
Date_ 20130911
Time 21.50
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 65
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 1290
DW 20.800 usec
DE 6.50 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6278572 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

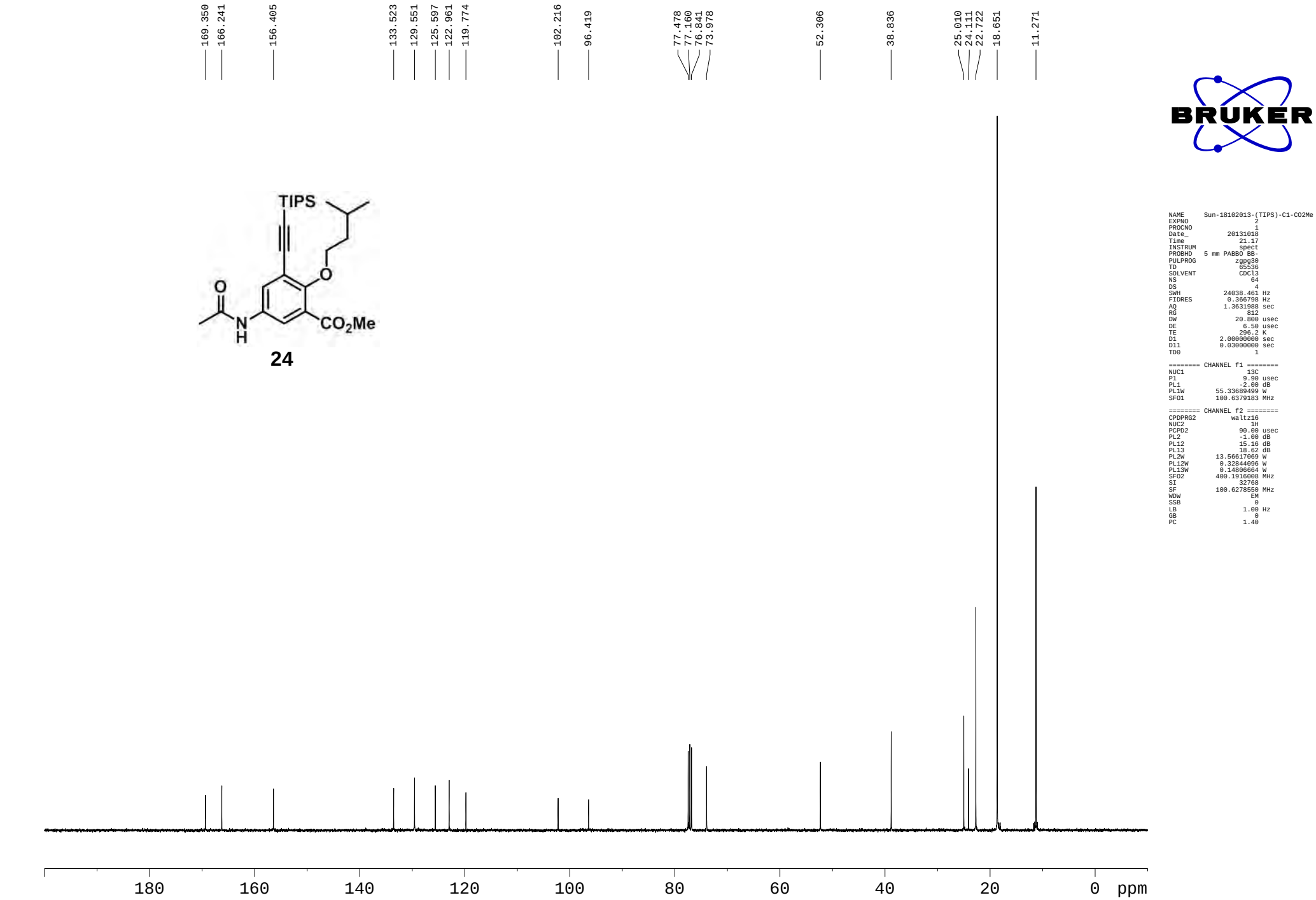
D:\MS_raw_data\hfc2116 06/17/14 11:14:37 AM (I, ic5)-C1-CO2Me
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc

hfc2116 #1-2 RT: 0.14-0.27 AV: 2 SM: 5G NL: 2.15E6
T: + p ESI Full ms [99.50-800.50]



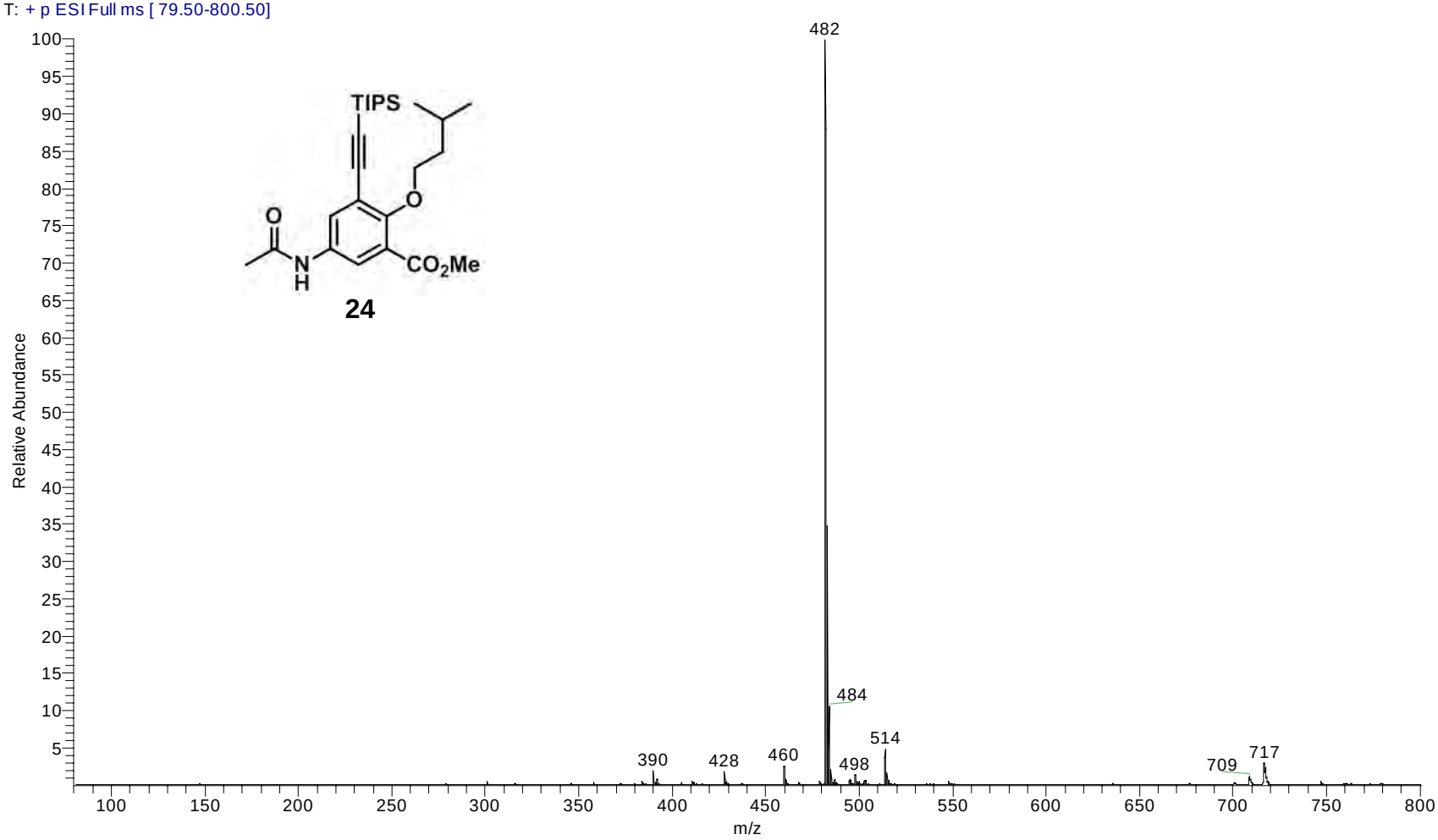
23

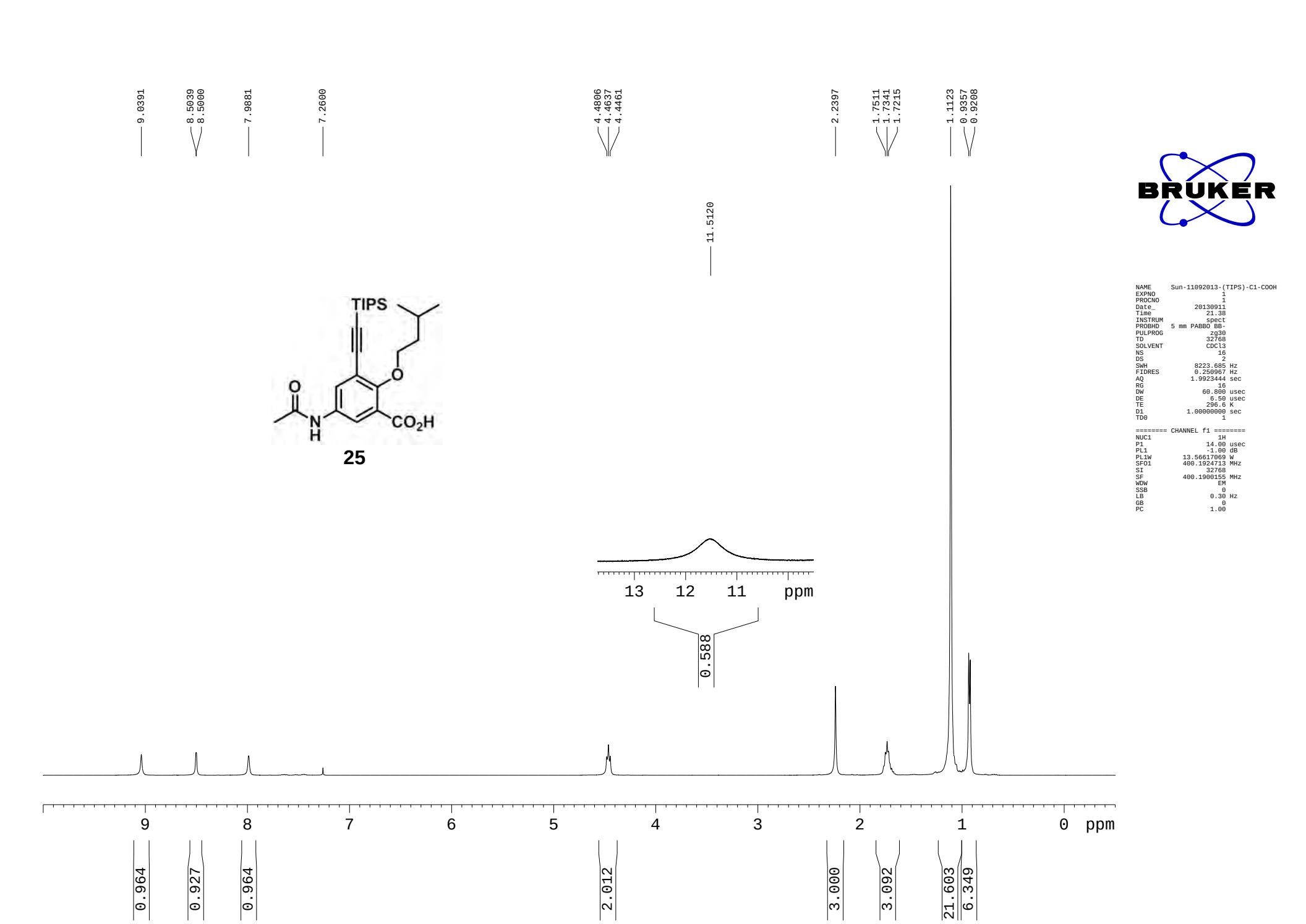

7.798
7.791
7.781
7.775
7.260
7.118
4.162
4.145
4.128
3.885
2.163
1.799
1.782
1.765
1.749
1.736
1.719
1.702
1.686
1.560
1.276
1.250
1.128
0.938
0.922
TIPS
O
O
N
H
CO2Me
24
BRUKER
NAME Sun-18102013-(TIPS)-C1-CO2Me
EXPNO 1
PROCNO 1
Date_ 20131018
Time 17.00
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 32
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 144
DW 60.800 usec
DE 6.50 usec
TE 296.1 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1900151 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
9
8
7
6
5
4
3
2
1
0
ppm
1.809
0.969
1.947
2.840
2.934
3.208
19.724
6.000

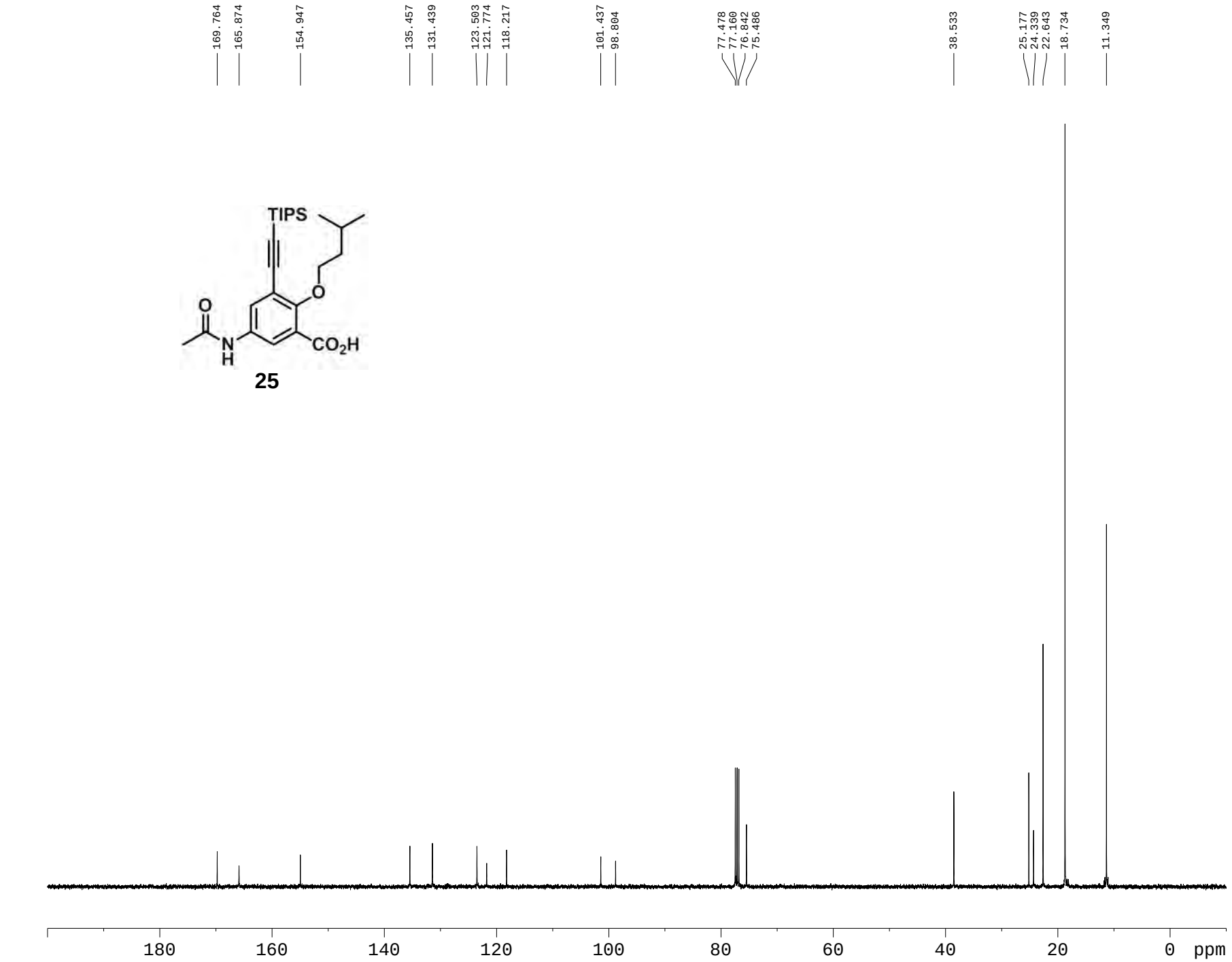

169.350
166.241
156.405
133.523
129.551
125.597
122.961
119.774
102.216
96.419
77.478
77.160
76.841
73.978
52.306
38.836
25.010
24.111
22.722
18.651
11.271
TIPS
O
O
N
H
CO2Me
24
NAME Sun-18102013-(TIPS)-C1-CO2Me
EXPNO 2
PROCNO 1
Date_ 20131018
Time 21.17
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 812
DW 20.800 usec
DE 6.50 usec
TE 296.2 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6278550 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

D:\MS_raw_data\hfc1993 08/28/13 02:17:04 PM (TIPS,ic5)-C1-CO2Me
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

hfc1993 #1-2 RT: 0.14-0.22 AV: 2 SM: 5G NL: 3.92E6
T: + p ESI Full ms [79.50-800.50]

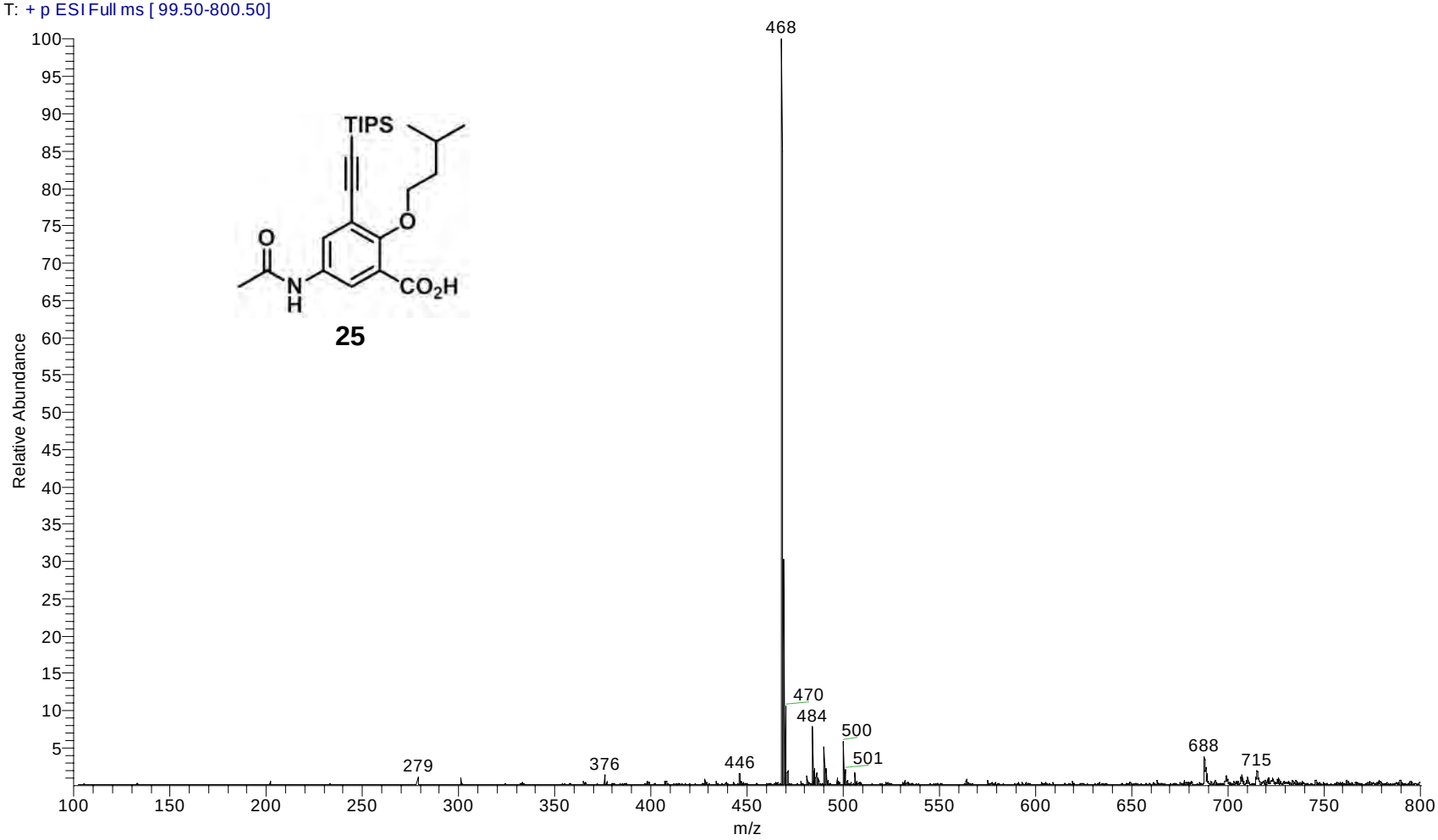


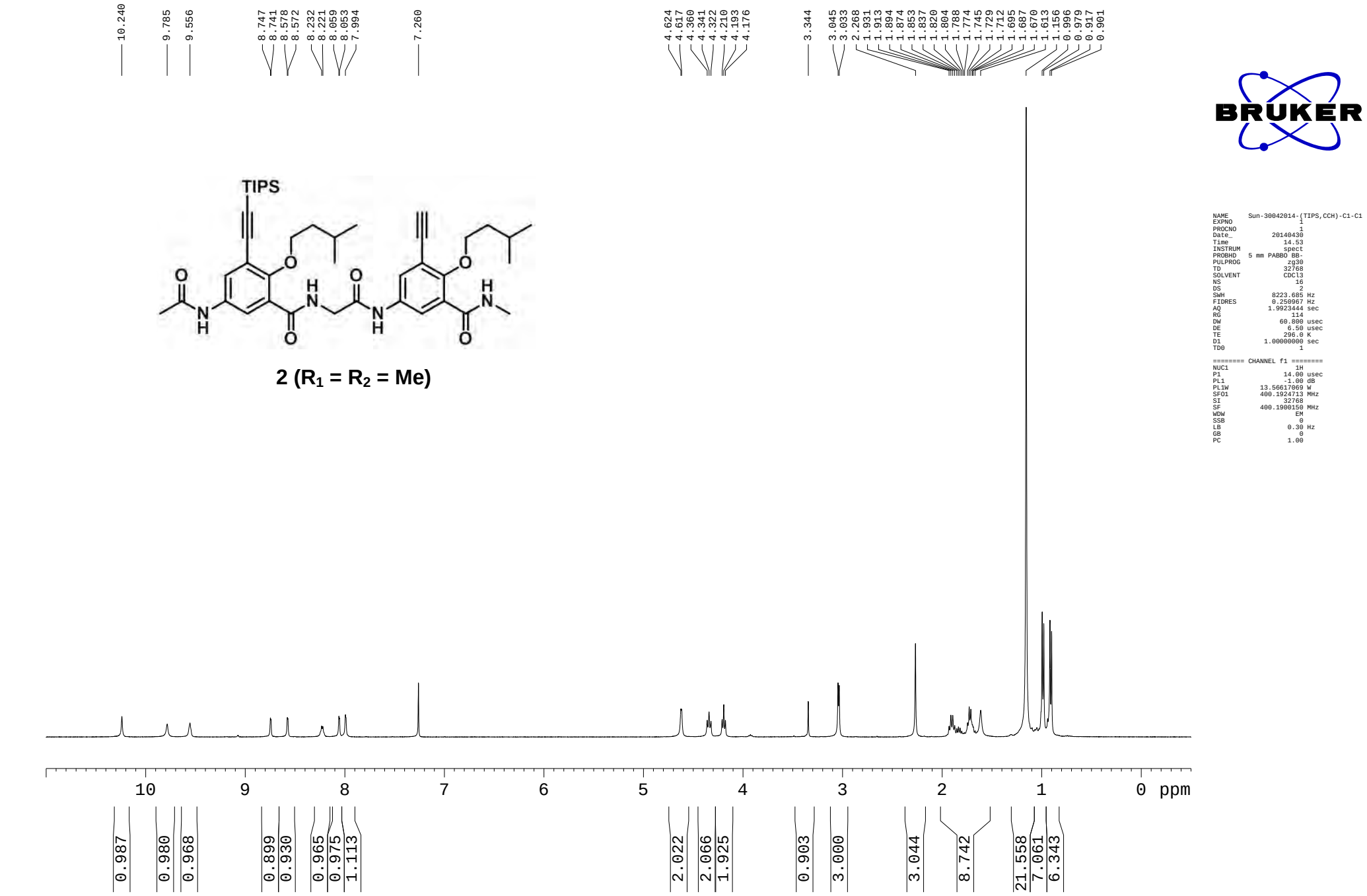

9.0391
8.5039
8.5000
7.9881
7.2600
4.4806
4.4637
4.4461
2.2397
1.7511
1.7341
1.7215
1.1123
0.9357
0.9208
11.5120
TIPS
O
O
N
H
CO2H
25
13
12
11
ppm
0.588
9
8
7
6
5
4
3
2
1
0
ppm
0.964
0.927
0.964
2.012
3.000
3.092
21.603
6.349
NAME Sun-11092013-(TIPS)-C1-COOH
EXPNO 1
PROCNO 1
Date_ 20130911
Time 21.38
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 16
DW 60.800 usec
DE 6.50 usec
TE 296.6 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1924713 MHz
SI 32768
SF 400.1900155 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00


169.764
165.874
154.947
135.457
131.439
123.503
121.774
118.217
101.437
98.804
77.478
77.160
76.842
75.486
38.533
25.177
24.339
22.643
18.734
11.349
TIPS
O
O
N
H
CO2H
25
BRUKER
NAME Sun-11092013-(TIPS)-C1-COOH
EXPNO 2
PROCNO 1
Date_ 20130911
Time 21.41
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 64
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 322
DW 20.800 usec
DE 6.50 usec
TE 296.9 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6278488 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

D:\MS_raw_data\hfc2115 06/16/14 05:32:43 PM (TIPS, ic5)-C1-COOH
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc

hfc2115 #10 RT: 0.85 AV: 1 SM: 5G NL: 1.11E6
T: + p ESI Full ms [99.50-800.50]

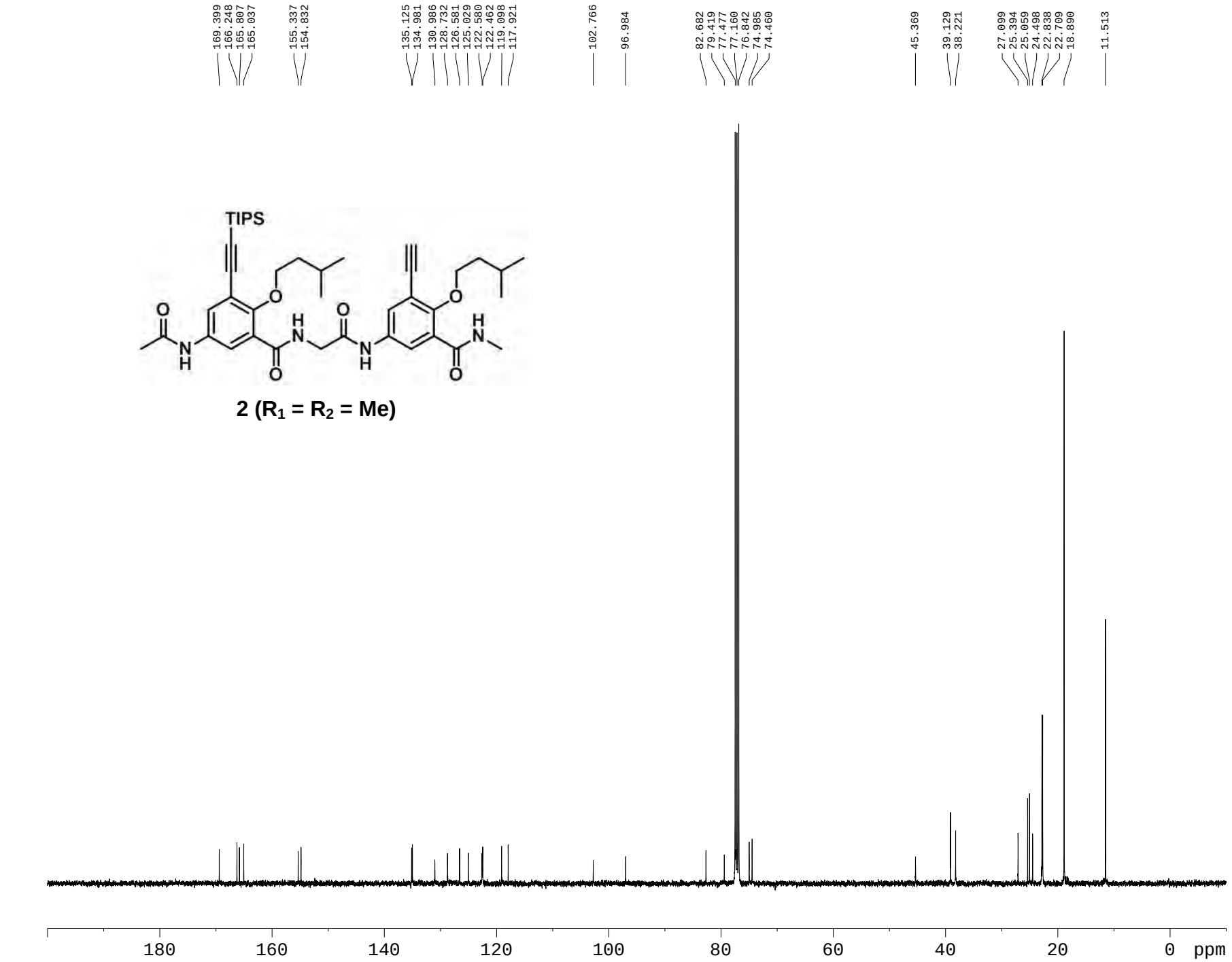




2 (R_1 = R_2 = Me)

BRUKER

```
NAME        Sun-30042014-(TIPS,CCH)-C1-C1
EXPNO                   1
PROCNO                  1
Date_            20140430
Time                14.53
INSTRUM             spect
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  32768
SOLVENT             CDCl3
NS                     16
DS                      2
SWH              8223.685 Hz
FIDRES           0.250967 Hz
AQ               1.9923444 sec
RG                    114
DW                60.800 usec
DE                 6.50 usec
TE                 296.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                14.00 usec
PL1                -1.00 dB
PL1W         13.56617069 W
SFO1         400.1924713 MHz
SI                  32768
SF           400.1900150 MHz
WDW                    EM
SSB                     0
LB                 0.30 Hz
GB                      0
PC                   1.00
```



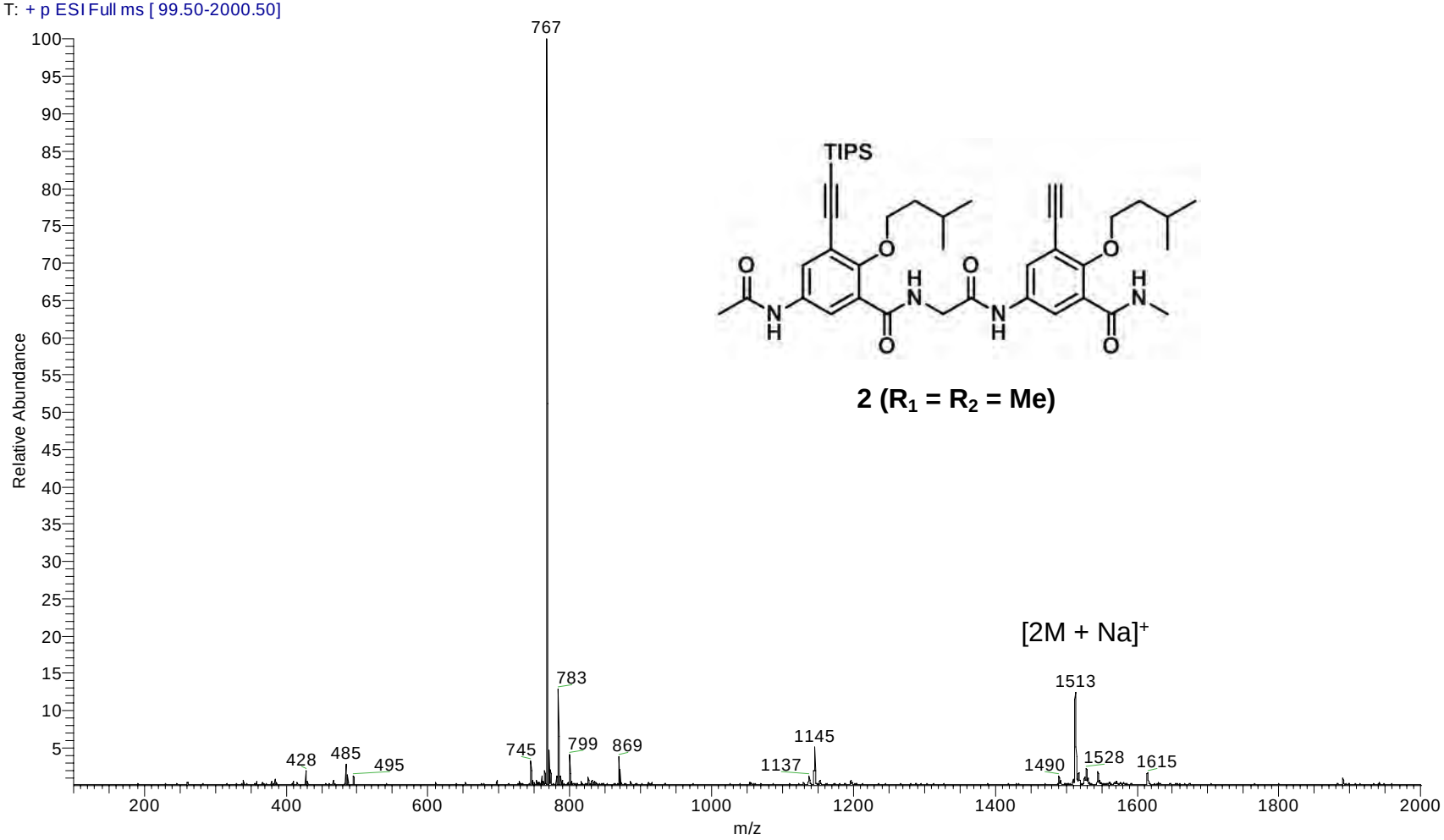
2 (R_1 = R_2 = Me)

BRUKER

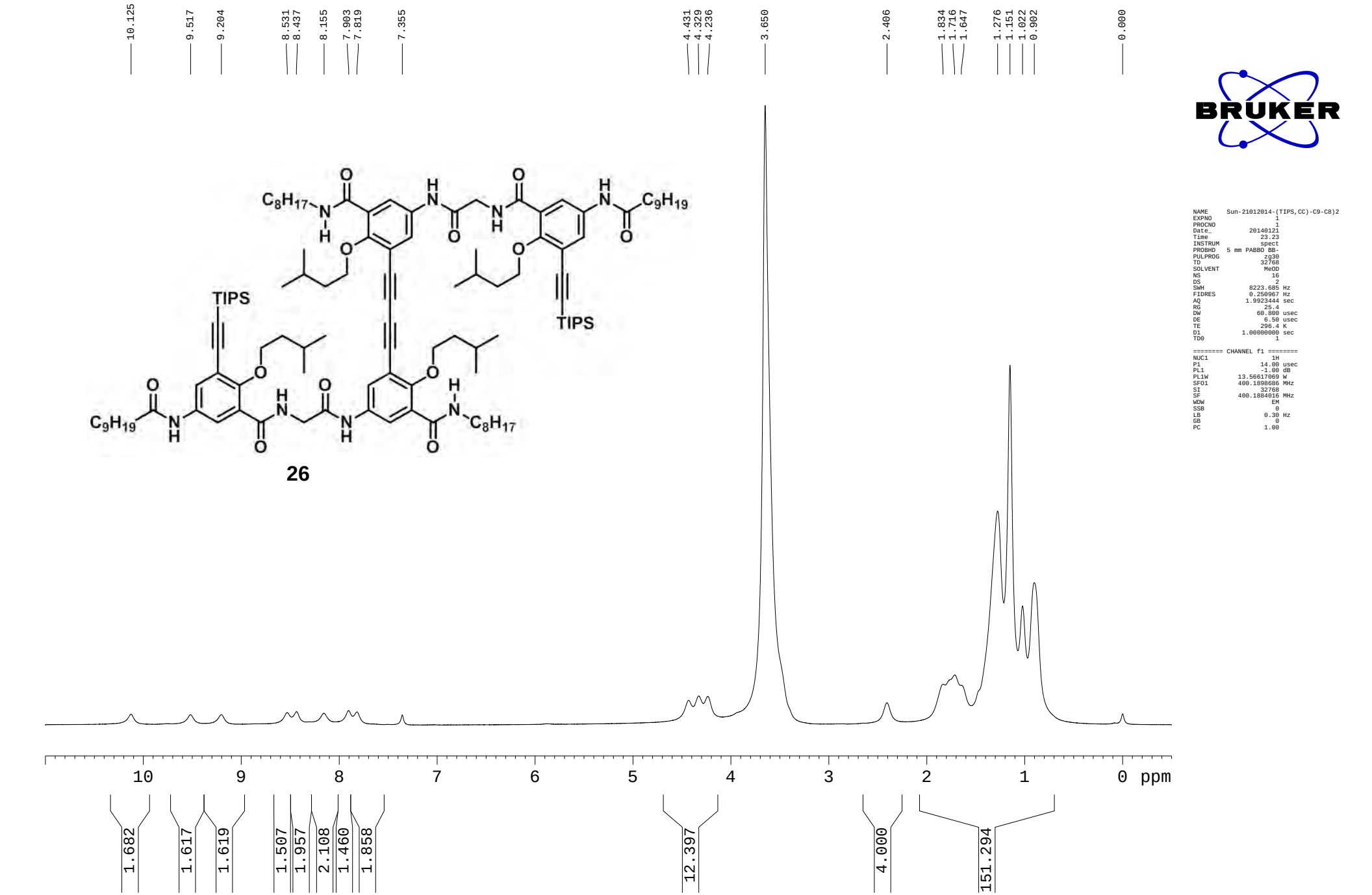
```
NAME          Sun-30042014-(TIPS,CCH)-C1-C1
EXPNO                  3
PROCNO                 1
Date_           20140430
Time                20.38
INSTRUM             spect
PROBHD   5 mm PABBO BB-
PULPROG           zgpg30
TD                 65536
SOLVENT            CDCl3
NS                  1147
DS                     4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ             1.3631988 sec
RG                   161
DW                20.800 usec
DE                 6.50 usec
TE                296.8 K
D1             2.00000000 sec
D11            0.03000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  13C
P1                   9.90 usec
PL1                 -2.00 dB
PL1W         55.33689499 W
SFO1         100.6379183 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2                90.00 usec
PL2                  -1.00 dB
PL12                 15.16 dB
PL13                 18.62 dB
PL2W         13.56617069 W
PL12W         0.32844096 W
PL13W         0.14806664 W
SFO2         400.1916008 MHz
SI                   32768
SF           100.6278446 MHz
WDW                    EM
SSB                    0
LB                  1.00 Hz
GB                     0
PC                  1.40
```

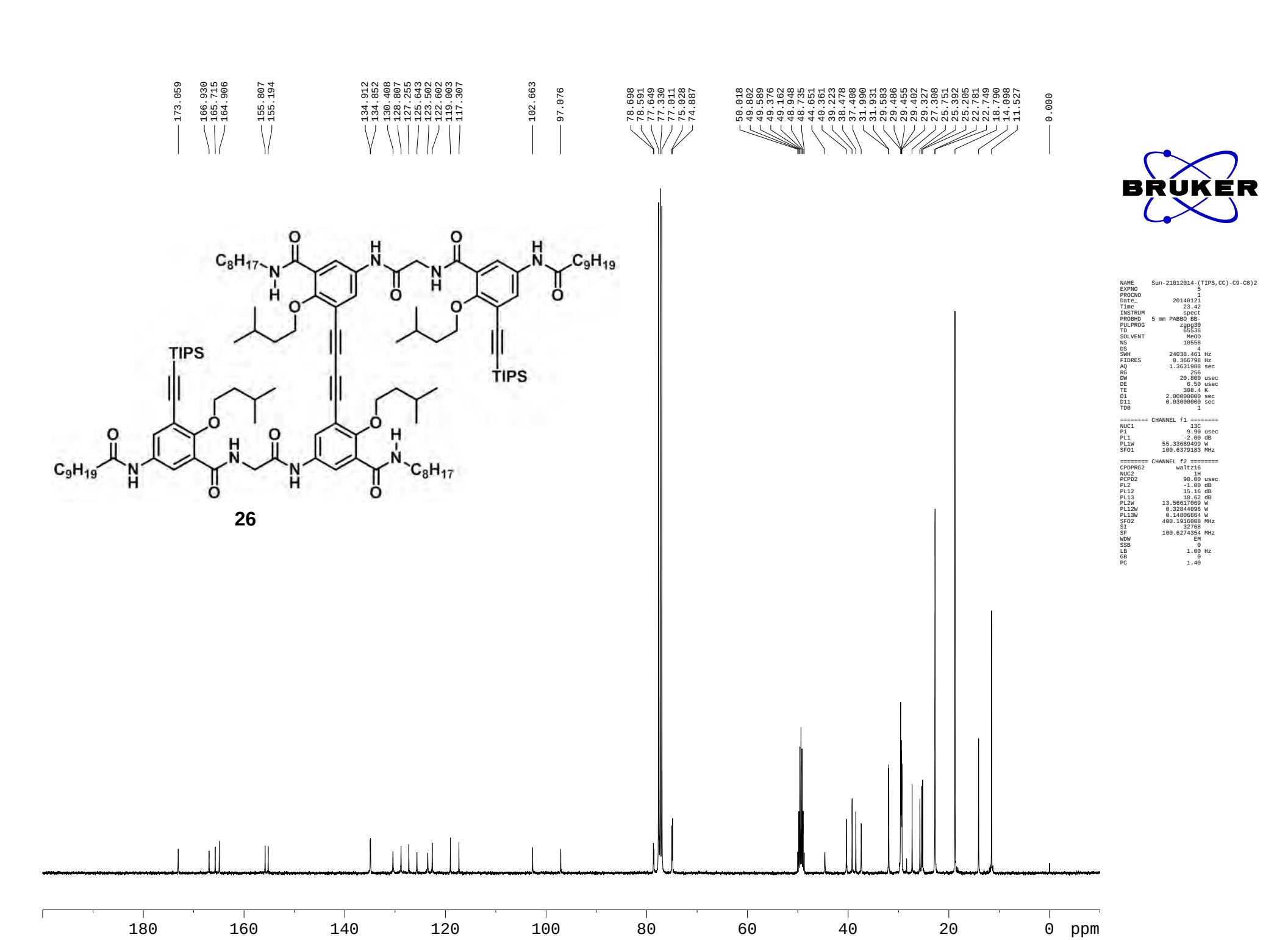
D:\MS_raw_data\hfc1997 09/09/13 01:59:43 PM (TIPS,CCH) C1-C1
esi pos, 3kV, 15ul/min, w/ sheath gas, unknown conc.

hfc1997 #2-4 RT: 0.26-0.44 AV: 3 SM: 5G NL: 8.91E5
T: + p ESI Full ms [99.50-2000.50]



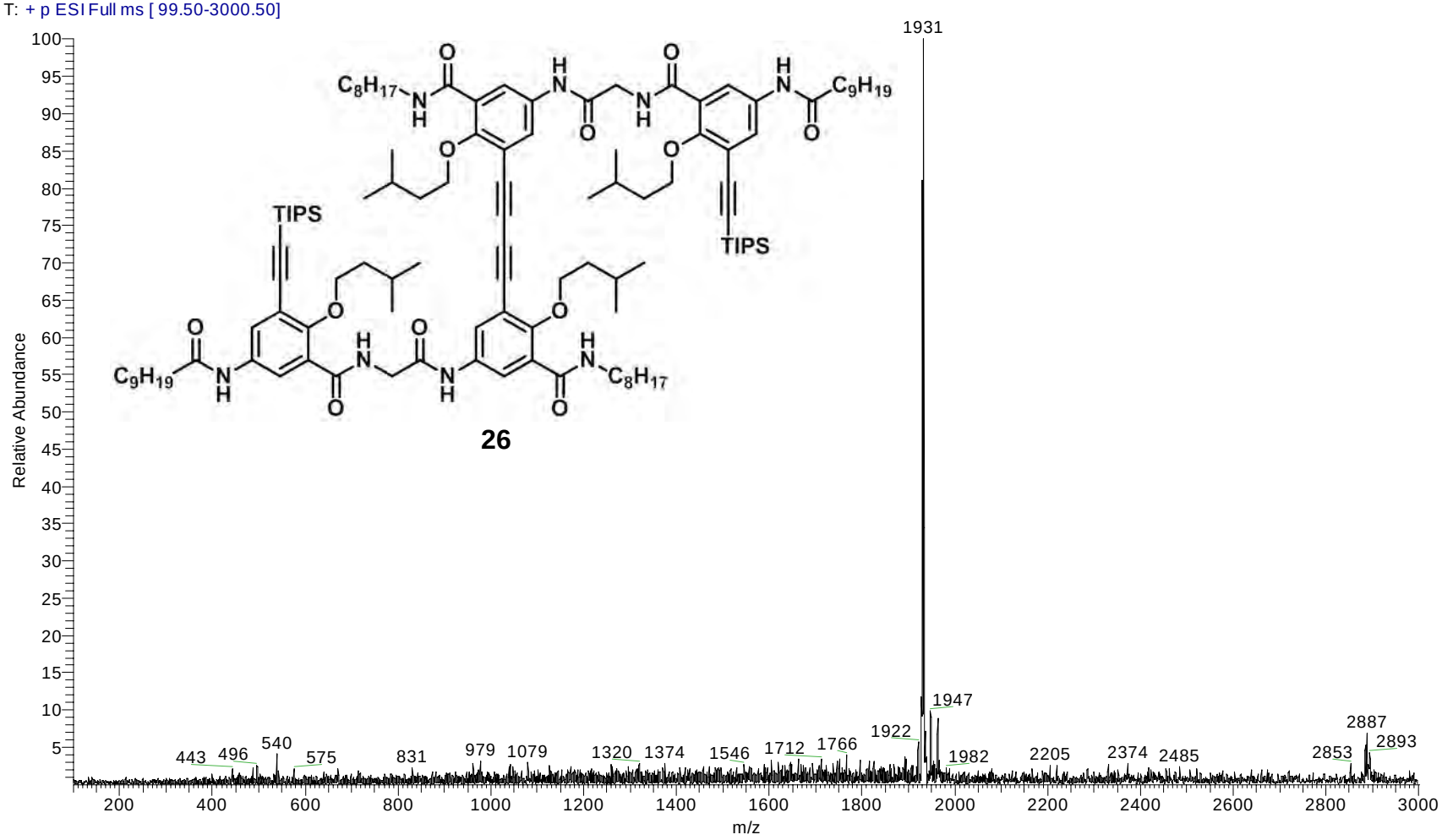
2 (R_1 = R_2 = Me)

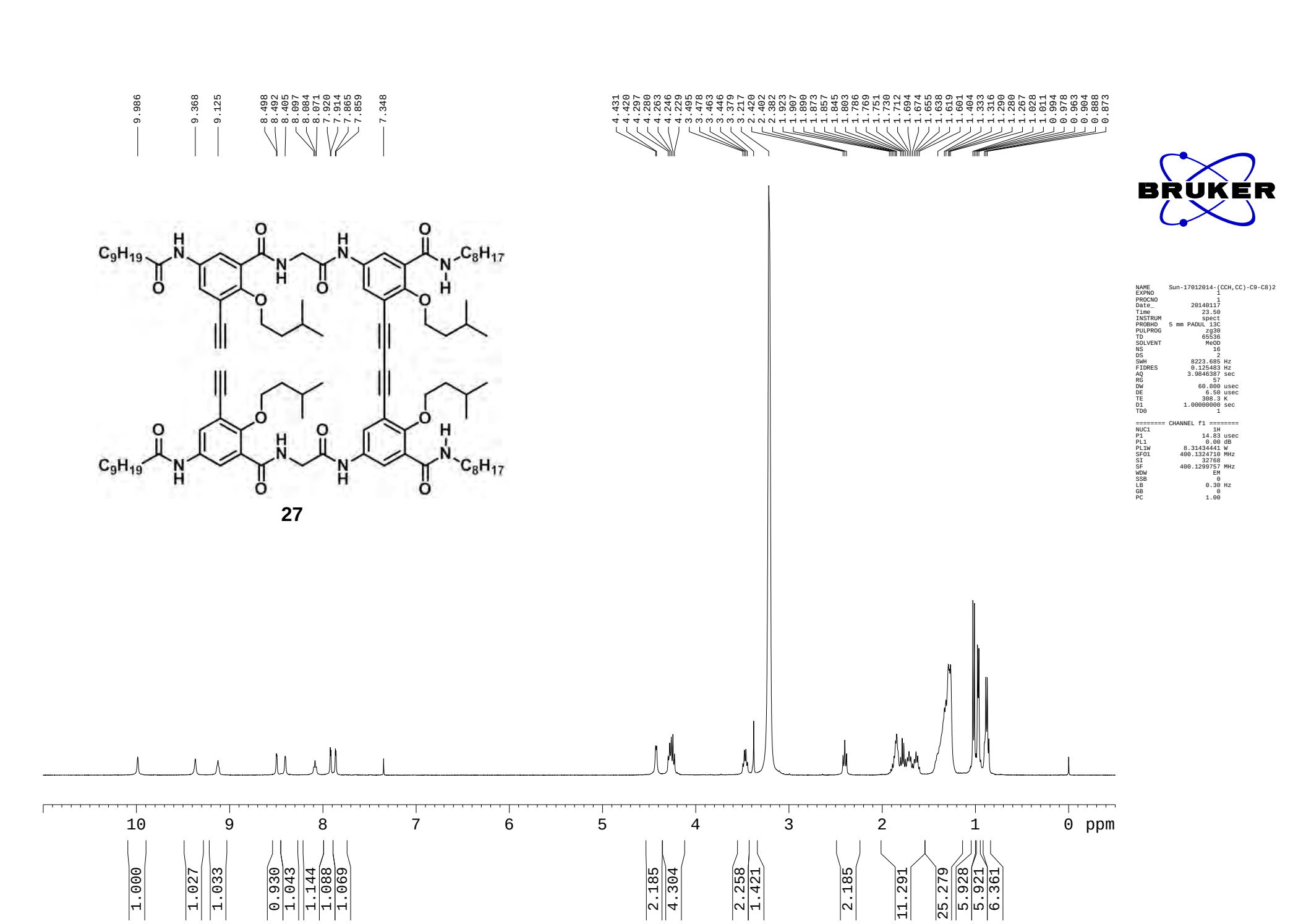

10.125
9.517
9.204
8.531
8.437
8.155
7.903
7.819
7.355
4.431
4.329
4.236
3.650
2.406
1.834
1.716
1.647
1.276
1.151
1.022
0.902
0.000
TIPS
TIPS
26
NAME Sun-21012014-(TIPS,CC)-C9-C8)2
EXPNO 1
PROCNO 1
Date_ 20140121
Time 23.23
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 32768
SOLVENT MeOD
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.250967 Hz
AQ 1.9923444 sec
RG 25.4
DW 60.800 usec
DE 6.50 usec
TE 296.4 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.00 usec
PL1 -1.00 dB
PL1W 13.56617069 W
SFO1 400.1898686 MHz
SI 32768
SF 400.1884016 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0 ppm
1.682
1.617
1.619
1.507
1.957
2.108
1.460
1.858
12.397
4.000
151.294


173.059
166.930
165.715
164.906
155.807
155.194
134.912
134.852
130.408
128.807
127.255
125.643
123.502
122.602
119.003
117.307
102.663
97.076
78.698
78.591
77.649
77.330
77.011
75.028
74.887
50.018
49.802
49.589
49.376
49.162
48.948
48.735
44.651
40.361
39.223
38.478
37.408
31.990
31.931
29.583
29.486
29.455
29.402
29.327
27.308
25.751
25.392
25.205
22.781
22.749
18.790
14.098
11.527
0.000
TIPS
TIPS
26
NAME Sun-21012014-(TIPS,CC)-C9-C8)2
EXPNO 5
PROCNO 1
Date_ 20140121
Time 23.42
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zgpg30
TD 65536
SOLVENT MeOD
NS 10558
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631988 sec
RG 256
DW 20.800 usec
DE 6.50 usec
TE 308.4 K
D1 2.00000000 sec
D11 0.03000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 13C
P1 9.90 usec
PL1 -2.00 dB
PL1W 55.33689499 W
SFO1 100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2 waltz16
NUC2 1H
PCPD2 90.00 usec
PL2 -1.00 dB
PL12 15.16 dB
PL13 18.62 dB
PL2W 13.56617069 W
PL12W 0.32844096 W
PL13W 0.14806664 W
SFO2 400.1916008 MHz
SI 32768
SF 100.6274354 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40
180
160
140
120
100
80
60
40
20
0
ppm

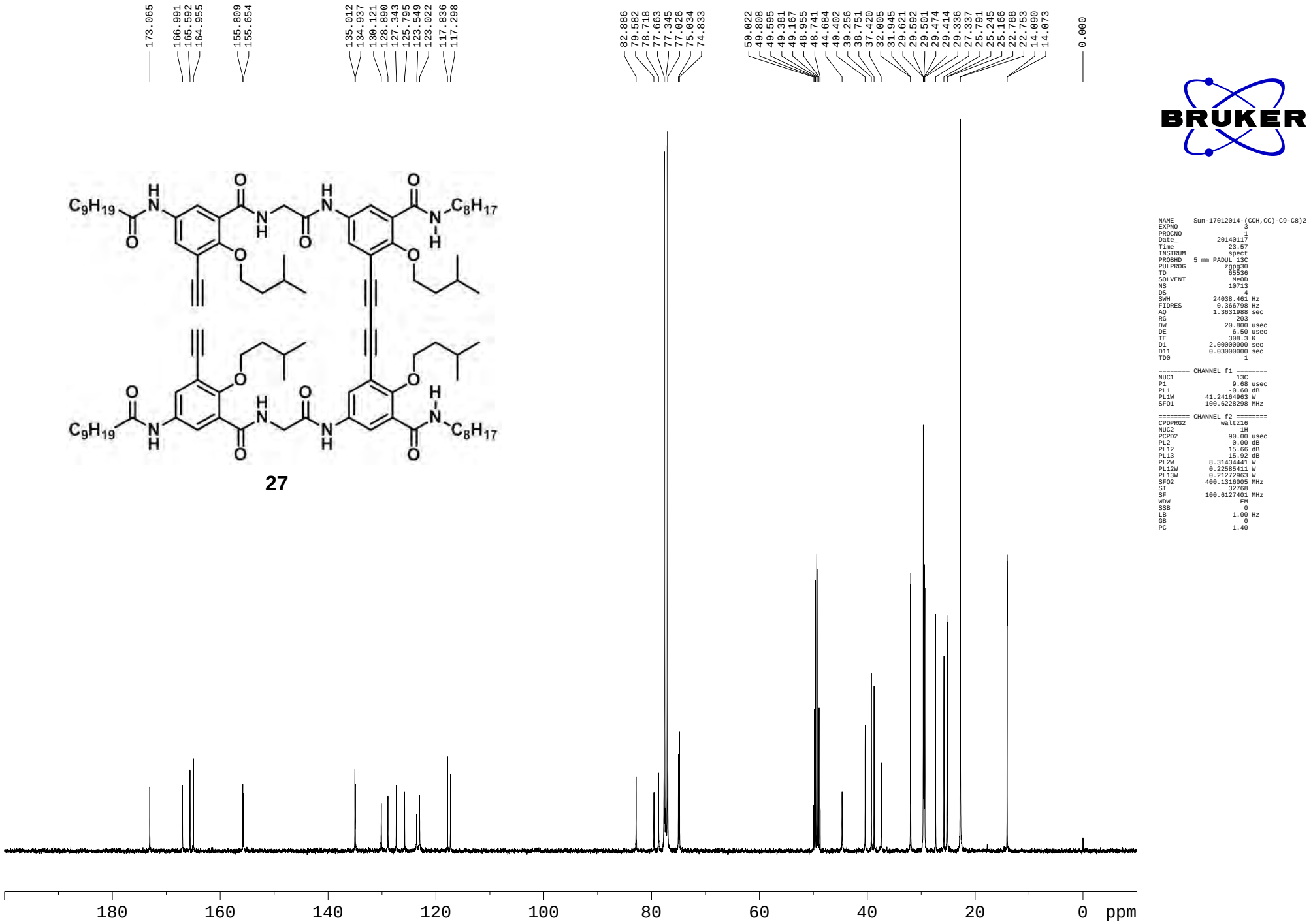
D:\MS_raw_data\hfc2028_131115152329 11/15/13 03:23:29 PM (TIPS,CC)-Cl-C8)2
esi pos, 3kV, 20ul/min, w/ sheath gas, unknown conc.

hfc2028_131115152329 #2-12 RT: 0.23-1.12 AV: 11 SM: 5G NL: 4.11E4
T: + p ESI Full ms [99.50-3000.50]




9.986
9.368
9.125
8.498
8.492
8.405
8.097
8.084
8.071
7.920
7.914
7.865
7.859
7.348
4.431
4.420
4.297
4.280
4.263
4.246
4.229
3.495
3.478
3.463
3.446
3.379
3.217
2.420
2.402
2.382
1.923
1.907
1.890
1.873
1.857
1.845
1.803
1.786
1.769
1.751
1.730
1.712
1.694
1.674
1.655
1.638
1.619
1.601
1.404
1.333
1.316
1.290
1.280
1.267
1.028
1.011
0.994
0.978
0.963
0.904
0.888
0.873
BRUKER
NAME Sun-17012014-(CCH,CC)-C9-C8)2
EXPNO 1
PROCNO 1
Date_ 20140117
Time 23.50
INSTRUM spect
PROBHD 5 mm PADUL 13C
PULPROG zg30
TD 65536
SOLVENT MeOD
NS 16
DS 2
SWH 8223.685 Hz
FIDRES 0.125483 Hz
AQ 3.9846387 sec
RG 57
DW 60.800 usec
DE 6.50 usec
TE 308.3 K
D1 1.00000000 sec
TD0 1
======== CHANNEL f1 ========
NUC1 1H
P1 14.83 usec
PL1 0.00 dB
PL1W 8.31434441 W
SFO1 400.1324710 MHz
SI 32768
SF 400.1299757 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00
10
9
8
7
6
5
4
3
2
1
0 ppm
1.000
1.027
1.033
0.930
1.043
1.144
1.088
1.069
2.185
4.304
2.258
1.421
2.185
11.291
25.279
5.928
5.921
6.361

27

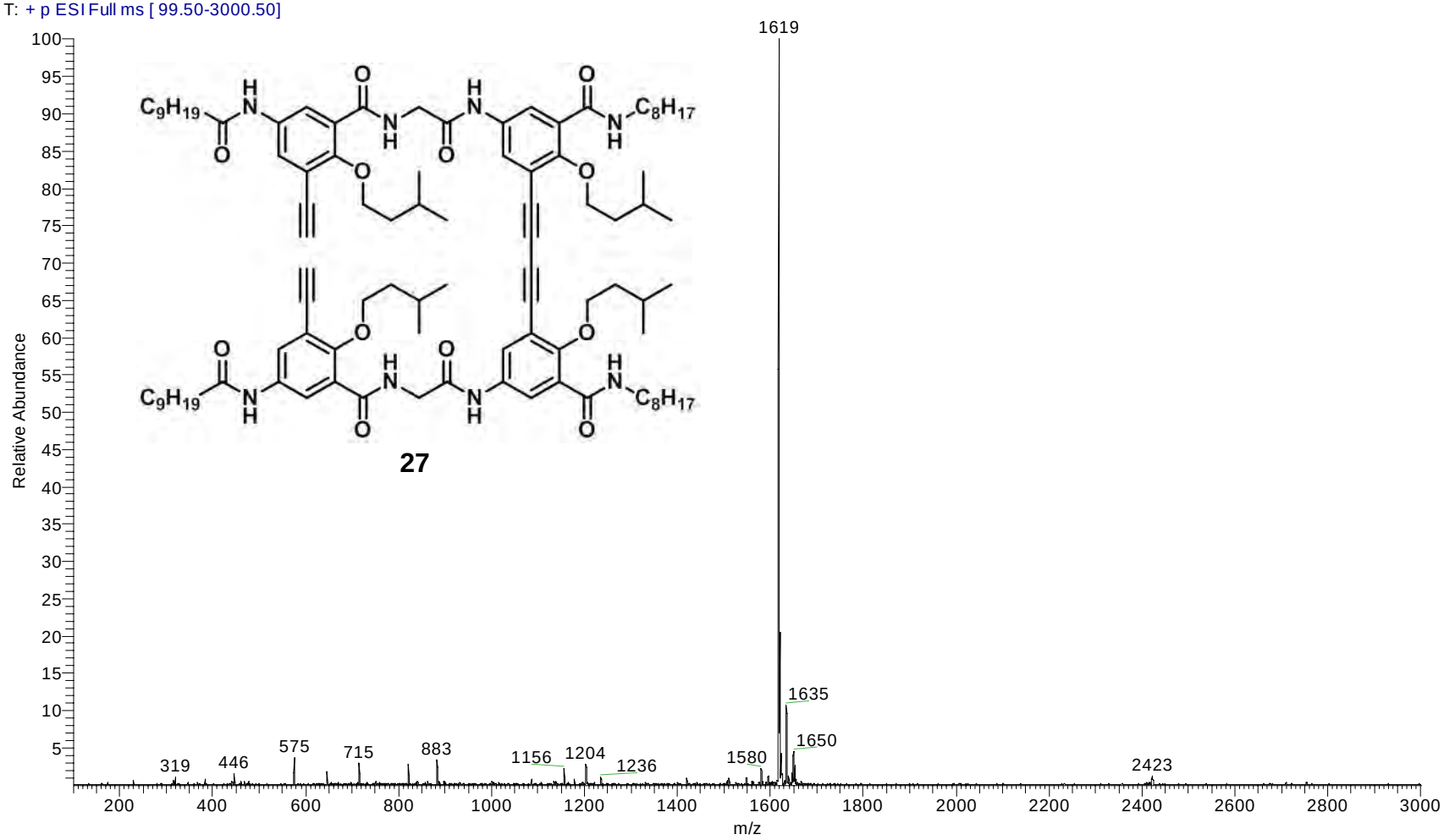


27

```
NAME          Sun-17012014-(CCH,CC)-C9-C8)2
EXPNO                                     3
PROCNO                                    1
Date_                              20140117
Time                                 23.57
INSTRUM                               spect
PROBHD       5 mm PADUL 13C
PULPROG                            zgpg30
TD                                   65536
SOLVENT                               MeOD
NS                                   10713
DS                                       4
SWH                           24038.461 Hz
FIDRES                         0.366798 Hz
AQ                             1.3631988 sec
RG                                     203
DW                                20.800 usec
DE                                 6.50 usec
TE                                   308.3 K
D1                           2.00000000 sec
D11                          0.03000000 sec
TD0                                      1

======== CHANNEL f1 ========
NUC1                                   13C
P1                                  9.68 usec
PL1                                -0.60 dB
PL1W                        41.24164963 W
SFO1                       100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2                         waltz16
NUC2                                   1H
PCPD2                              90.00 usec
PL2                                 0.00 dB
PL12                               15.66 dB
PL13                               15.92 dB
PL2W                         8.31434441 W
PL12W                        0.22585411 W
PL13W                        0.21272963 W
SFO2                       400.1316005 MHz
SI                                   32768
SF                         100.6127401 MHz
WDW                                    EM
SSB                                     0
LB                                 1.00 Hz
GB                                      0
PC                                 1.40
```

D:\MS_raw_data\hfc2062 01/20/14 02:54:45 PM (TIPS,cc)-C9-C8)2
ESI pos, 3kV, 15uL/min, w/ sheath gas, unknown conc.

hfc2062 #1-9 RT: 0.16-0.87 AV: 9 SM: 5G NL: 3.70E5
T: + p ESI Full ms [99.50-3000.50]



27